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VOLUME 27 JULY 11, 1938 NUMBER 14

CONTENTS OF THIS ISSUE

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

Proceedings of
American Association of Textile Chemists and Colorists

Bibliography on the Chemistry of Wool—concluded.. P361
Arthur L. Smith and Milton Harris

Communication:
The Keratin Fibers..... P393
Wm. Harrison

Official Publication of the American Association of Textile Chemists and Colorists

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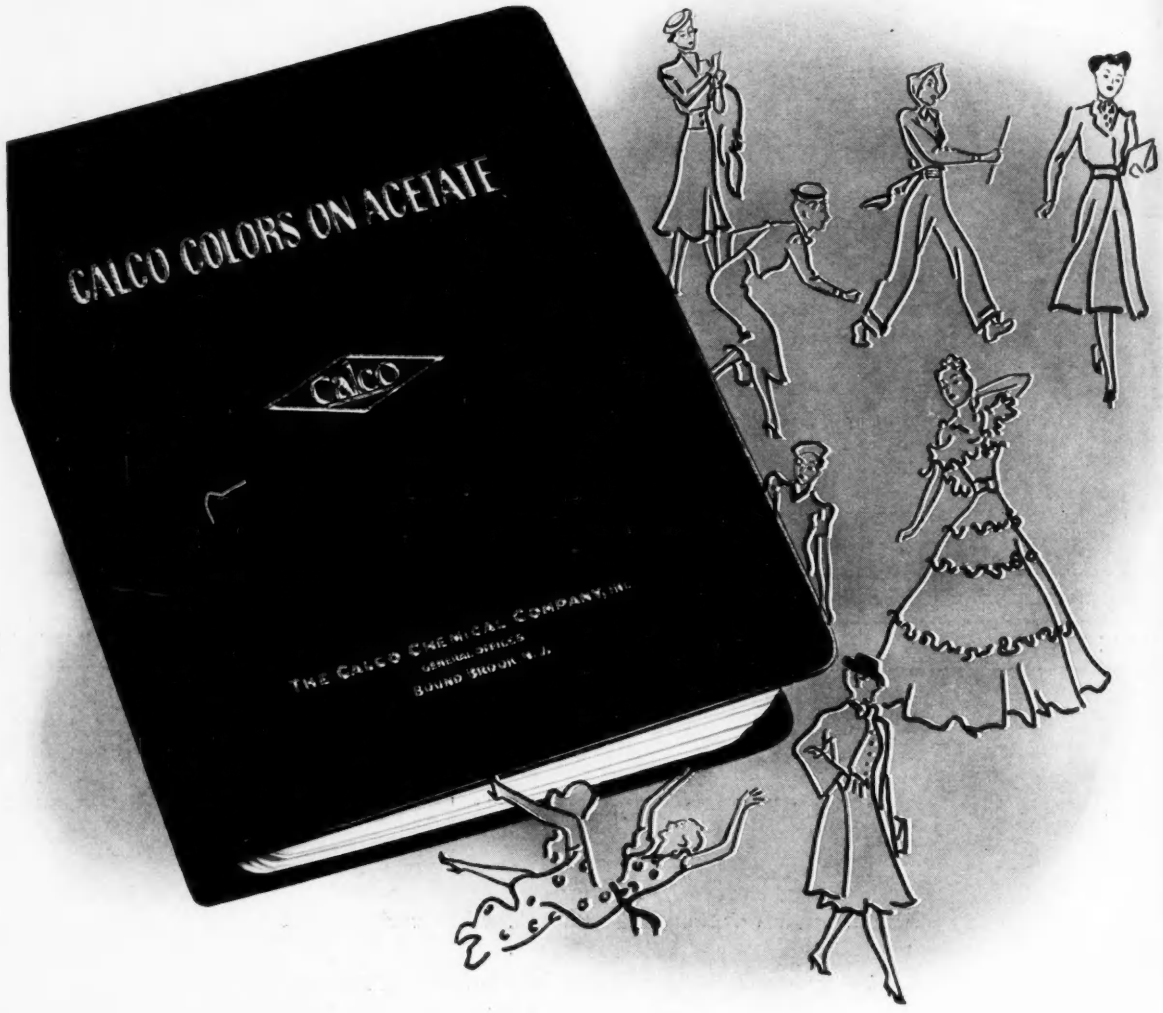

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PROCEEDINGS OF THE

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July 11, 1938

Quarterly Research Number

Number 5

Contents

Bibliography on the Chemistry of Wool—Concluded. P363
Arthur L. Smith and Milton Harris

Communication:
The Keratin Fibers..... P393
Wm. Harrison

AMERICAN DYESTUFF REPORTER

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Bibliography on the Chemistry of Wool*

(Concluded from April 4, 1938 Quarterly Research Number)

ARTHUR L. SMITH and MILTON HARRIS

INTRODUCTION

THIS bibliography is limited to publications dealing principally with the more fundamental aspects of the chemistry of wool. Publications relating to industrial processes and to physical testing have been included only if they bear upon the interpretation of chemical properties. Although it has been necessary to exercise personal judgment in the selection of papers to be included, no paper has been excluded because of the doubtful validity of the data or theories given in it. The chief sources of material were Chemical Abstracts, British Chemical Abstracts, and Chemisches Zentralblatt, and wherever possible, abstracts were taken directly from these journals.

The bibliography has been compiled as part of a program of research on the chemistry of wool which is being done at the National Bureau of Standards for the American Association of Textile Chemists and Colorists under the Research Associate plan.

ACKNOWLEDGMENTS

We wish to acknowledge the financial aid given this work by the Textile Foundation, Incorporated, the Chemical Foundation, Incorporated, and the Eavenson & Levering Company. We also wish to express our appreciation to Mr. Alban Eavenson, Chairman, and the other members of the Committee on the Chemistry of Wool, American Association of Textile Chemists and Colorists, for their helpful suggestions.

* Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce.

CONTENTS†

Acid, Absorption of
  Determination of
  Effect of
Alkali, Absorption of
  Determination of
  Effect of
Amino Nitrogen
Bacteria, Enzymes and Fungi
Bromination
Carbonizing
Chemical Constitution
  Amino Acids
  Intermediate Hydrolytic Products
  Nitrogen
  Sulfur
Chlorination
Cystine
Damage, Determination of
Deamination, Amino Nitrogen
Dielectric Constant
Dyeing, Mordant
  Theory of
Elastic Characteristics
Electrokinetic Properties
Enzymes
Felting
Fibers, Determination of, in Mixtures
Fulling
Fungi
Halogenation
Heat, Effect of
Heat of Combustion
Heat of Hydration
Heat of Neutralization
Isoelectric Point
Light, Effect of
Milling
Miscellaneous Reagents, Effect of
Moisture, Absorption of
  Determination of
  Effect of
Molecular Weight
Mordanting (Dyeing)
Nitrogen
Oxidation
Photochemical Decomposition
Reduction
Specific Gravity
Specific Heat
Structure
Sulfur
Swelling
Tanning
X-Ray

†The contents indicate the complete bibliography. The first portion appeared in the April 4, 1938 Quarterly Research Number; the remainder appears in this issue.

147.—Changes Undergone by Wool Hairs During the Whole Manufacturing Process Up to the Finished Dyed Fabric.

P. Krais, H. Markert and O. Viertel. *Forschungsh. deut. Forsch.-Inst. Textilind. Dresden 14*, 73 pp. (1933); *Chem. Zentr.* 1933, II, 2211-12. After a detailed consideration of the mechanical properties of the wool fibers, methods for testing them chemically are considered. Soluble nitrogen (characterized as injurious) is determined by the Kjeldahl method in material which has been treated with potassium hydroxide and hydrogen peroxide. In many manufacturing processes the sulfur content of the fibers is decreased, often with accompanying deterioration of the fibers. The sulfur content is determined in hydrochloric acid solution by the use of Benedict-Denis solution (25 g cupric nitrate, 25 g sodium chloride and 10 g ammonium nitrate in 100 ml water). The dichromates which are reduced by 0.5 per cent sodium carbonate solution in which 1 g of wool has been soaked, increases continuously during the process of working up the wool. The "Allworden" reaction (treatment of the wool with saturated chlorine water) showed no difference between treated and raw wools. The behavior of finished yarn was no different from that of raw wool toward dyeing with methylene blue. Since these methods offered no sufficiently sensitive distinction between good and deteriorated wools, others were tried. In titration with sulfuric acid, wools deteriorated by alkalies showed the highest acid consumption, those deteriorated by acids the lowest. In oxidation with 0.1 *N* iodine solution, the latter wools gave the highest iodine number, the former the lowest. The wools absorbed up to 6 per cent sulfuric acid from acid dye of baths (dye ratio 1: 30), acid-treated wools absorbing least, alkali-treated most. Wools deteriorated by acids showed characteristic bubble formation, etc., under the microscope. Only absorption and swelling are suitable for the detection of very slight deterioration. All methods were carefully checked for their usefulness in textile technic.

148.—The Estimation of Damage on Chlorinated Knitted Wool Fabrics.

C. H. Edwards. *J. Textile Inst. 24,* T1-9 (1933).

149.—Determination of Soluble Nitrogen in Wool According to Sauer's Method.

R. Folgner and G. Schneider. *Monatschr. Textil-Ind. 49,* 181-2 (1934). Treat 0.5 g of wool in a 200-ml flask with 50 ml of 2 per cent hydrogen peroxide 10 ml of 0.5 *N* potassium hydroxide and 40 ml of water. Shake the mixture well, let stand for 24 hours in a thermostat at 25° and then vigorously shake for 3 hours. Dilute the mixture to the mark and filter through an ordinary filter. Discard the first 30 ml. Determine nitrogen in the next 100 ml by the Kjeldahl method.

150.—Iodine Number of Wool: A Method for Determining the Action of Various Chemical Reagents on Wool and Other Proteins.

M. Harris, H. A. Neville, and W. C. Fritz. *B. S. J. Research 12,* 803-9 (1934) RP689. The iodine number provides a qualitative measure of the extent to which the amino groups are affected by various treatments of the protein. Amino acids and proteins exhibit iodine numbers as determined by the standard method. The iodine numbers of such substances do not indicate ordinary unsaturation, but are shown to be related to the free amino nitrogen content. The iodine numbers of some typical proteins are reported and a general correspondence between the iodine numbers and the isoelectric point of the proteins is shown. Conversion of amino groups to hydroxyl groups, combination of amino groups with strong acids and other chemical reactions which affect the amino groups reduce the iodine numbers of amino acids (with the exception of cysteine) to zero. Part of the iodine number of wool is due to cystine, which is very susceptible to oxidation. The iodine number of wool is, therefore, affected by reactions of chemical reagents with the amino or the cystine groups.

151.—The Iodine Number of Wool.

R. W. McKay. *Am. Dyestuff Reptr. 23,* 697-8 (1934). This work was included in an investigation of the reactions of chlorine and related substances on wool in producing an unshrinkable finish. The stoichiometrical relations found by Harris, Neville and Fritz between the iodine number and free amino nitrogen are shown to be of an accidental nature. Wool samples treated with nitrous acid do not show a constant difference in iodine number from untreated samples when soaked in Wijs solution under the same conditions.

152.—Methylene Blue Absorption as a Quantitative Measure of Wool Damage.

R. E. Elmquist and O. P. Hartley. *Textile Research 5,* 149-56 (1935). The absorption of methylene blue from buffered solutions is proposed as an index to wool deterioration since it can be measured quantitatively by a simple titrimetric procedure. Experimental results are given for material damaged progressively under controlled conditions of laundering and for fabrics containing wools of different grades and different dyeings. A linear relationship exists between absorption and tensile strength. The reworked wool that was tested absorbed nearly four times as much methylene blue as the new serge used in the experiments. Optimum test conditions were determined and are discussed critically.

153.—Chemical Investigation of Faults in Wool Fabrics.

H. R. Hirst. *Textile Mfr. 61,* 32-3 (1935). The use of methods which are derived independently of a knowledge of the processing of the fabrics is described to diagnose faults resulting from chemical damage to wool or staining. Pauli's reagent and dyes that indicate the inner structure of wool fiber are useful agents, as also are neocarmine dyes which give distinctly different colors for various fibers.

154.—Physicochemical Methods for the Determination of Damages to Wool.

A. Itkina and Plechan. *Melliand Textilber. 16,* 45-6, 106-8 (1935). Instead of the customary determination of the reduction in tensile strength as a measure of the damage to wool fibers, the following methods are suggested: (1) The modified Pauli test. This uses more wool (0.2 to 1.0 g.) *M*-nitro-*O*-anisidine instead of sulfanilic acid. The standard solution is prepared by dissolving 0.008 g of tyrosine in 5 ml of 9 per cent sodium hydroxide solution. To this is added 0.2 g of diazotized *M*-nitro-*O*-anisidine dissolved in 5 ml of water. The resulting solution is diluted to 25 ml and heated for 5 minutes on a steam bath. The concentration of the standard solution is 0.0612 per cent of azo dye. (2) The absorption of dye. This test is made by dyeing the wool with a known concentration of methylene blue or benzopurpurin and determining the amount of dye left in the bath. The more the wool is damaged the greater is the amount of dye absorbed. (3) The effect of chlorine water. This is used as a qualitative test but can be adapted to quantitative work. (4) The swelling of wool fibers. Wool fibers are immersed in water for 10 minutes at 16 to 17° and their widths measured under a microscope. The greater the width, the greater is the damage of the preceding treatment. (5) The loss in weight. This is proportional to fiber damage. (6) The loss in nitrogen. The amount of nitrogen going into the treating liquor owing to the hydrolysis of wool can also be determined and used as an indication of the damage. Tables are given showing the results obtained by the various methods.

155.—Various Problems in the Examination of Wool Materials.

W. Schramek. *Monatschr. Textil-Ind. 50,* 189-92 (1935). In a study of the damage to wool caused by chemicals it was found that the so-called qualitative rapid methods, such as the Allwörden reaction, the dyeing with methylene blue, and the Markert-Krais-Viertel (M.K.V.) reaction, are either not sufficiently sensitive or are unsuitable for the testing of the action of alkali on wool and hair or give entirely contradictory results. The diazo reaction of Pauli and Binz (P.B.) is the only rapid method which gives a sure indication of the chemical damage of the wool fiber. The method is briefly stated together with certain precautions that must be observed. The M.K.V. and the P.B. reactions were used to study the effects of (1) a normal wool wash with soda, (2) a wool wash with a synthetic alkali-free detergent and (3) a wool wash with benzine. Tests showed that the M.K.V. method was unsuitable for the determination of alkali damage and that after exposure for 15 minutes the method yielded no difference in the appearance of 3 washed samples from the raw material. The P.B. reaction, however, showed that the alkaline wash had a decided action upon the wool, while the neutral synthetic detergent and the benzine had no appreciable effect on the dyeing. In order to determine whether the process of refining would bring out the pre-damage of the wool, tests were made in which the three test samples were boiled for 1 hour in a dilute acid solution of the usual concentration of the dye liquors, rinsed, neutralized with ammonia, washed, and carefully dried. The M.K.V. reaction showed no difference, even after the acid treatment, between the alkaline and the neutral prewashed wool material, while the sample washed with benzine showed a decided acid damage. The P.B. reaction showed that the maximum damage occurred where the wool had been pre-damaged in the wash. This variance in the results obtained with the M.K.V. reaction may be due to the fact that the wool washed with benzine is freer from fat and hence more extensively affected by the strong alkaline agent than is a wool with a higher fat content. In studying the resistance to wear, microscopic investigations were made of wool hairs from a coat sleeve which had been subjected to the ordinary wear and tear and

of wool which had been subjected to a wear-testing apparatus. The results of numerous tests show that the two types of exposures give comparable results and that the wear test corresponds to the process of actual usage.

156.—The Cause of the Von Allwörden Reaction.

K. Stirm and H. Collé. *Melliand Textilber. 16,* 585-6 (1935). On treating wool with bromine water, 26% of the total cystine and 39% of the total tyrosine go into solution. Similar treatment with chlorine water caused only 1.91% of the total cystine to go into solution. The amino acids, cystine and tyrosine, split off, swell up and dissolve, and cause the von Allwörden reaction.

157.—Testing of the Physical and Chemical Properties of Wool by Means of the Microscope.

W. v. Bergen. *Rayon Textile Monthly 16,* 527-9, 599-602, 553-5, 673 (1935); *Proc. Am. Soc. Testing Materials 35,* Pt. 2, 705-26 (1935). The microscopic appearance of wool (including kemp) fibers in longitudinal and cross sections are described and illustrated. The equipment and technic required for determining the fineness of wool fibers by the width, cross section, and gravimetric methods are described. The effect of sunlight on wool can be determined by measuring the width of the fiber before and after swelling with caustic soda. The actions of hydrogen peroxide, chlorine, alkalies, acids, mildew, and bacteria on wool are described and suggestions are given on methods to use for determining the amount of damage from these causes.

158.—The Treatment of Wool by the Halogens and D'Allwörden's Reaction.

A. Baron. *Rev. gen. mat. color. 40,* 171-2 (1936; cf. Ibid. *40,* 86 (1936). Von Allwörden's reaction is not questioned, but the hypothesis of Sturm and Colle is not upheld. The study should be based on two factors (a) the action of chlorine on keratin and (b) the action of chlorine on elasticum.

159.—Fiber Surface Studies. Can Even the Slightest Damage to Wool Fibers Be Made Visible?

H. Reumuth and H. Schwerdtner. *Z. ges. Textil-Ind. 39,* 12-18 (1936). Microscopic methods of examination of fiber are described and an improved method is developed. Photomicrographs show the results obtained by this method on a variety of wool fibers.

See 33, 6, 98, 126, 129, 264, 271, 272, 277, 281, 282, 283, 291, 342, 352, 353, 354.

DEAMINATION (Amino nitrogen).

See 25, 32, 34, 93, 103, 202, 206, 210, 221, 266, 170, 285, 290, 310, 311, 336, 386, 387.

DIELECTRIC CONSTANT

160.—Determination of the Dielectric Constant of Wool.

F. W. Holl, *Helv. Chim. Acta 19,* 281-3 (1936). The dielectric constant of washed, fat-free wool was determined by the bridge null method, by measuring the capacity of a cylindrical condenser filled first with air and then with the wool. The space occupied by the wool was calculated from its density (1,305) and the space occupied by air subtracted from this. The average value found was 4.56.

DYEING, Mordanting.

161.—The Theory of Dyeing. III.

Wilder D. Bancroft. *J. Phys. Chem. 18,* 385-437 (1914).

162.—Theory of Dyeing. IV.

W. D. Bancroft, *J. Phys. Chem. 19,* 50-64 (1915). This is a review of the literature.

163.—Mordants. III. Chrome.

W. D. Bancroft. *J. Phys. Chem. 26,* 736-72 (1922). Wool adsorbs $H_2Cr_2O_7$ from dichromate solution, and this is reduced to chromic oxide which is the mordant. Within limits the adsorption of $H_2Cr_2O_7$ is increased by increasing the acid concentration. $H_2Cr_2O_7$ oxidizes organic acids more readily in the presence of wool. Sulfuric acid is more effective than hydrochloric or nitric acid in causing the oxidation of wool by $H_2Cr_2O_7$. There is no appreciable oxidation of wool when oxalic, lactic, or formic acid is used as an assistant. A basic sulfate is first formed when wool is mordanted from chrome alum, but the former changes later to chromic oxide. Silk adsorbs chromic oxide less strongly than wool. Cotton takes up no chromic oxide from chrome alum, but it adsorbs the oxide from an alkaline solution. There is no evidence of any definite compound being formed when wool is mordanted with chromic oxide.

164.—Quinone ($C_6H_4O_2$).

H. Mercier. *Tiba* (Rev. teint. imp. bl. appr.) No. 3, 185-98 (March, 1923); *Chimie et industrie 11,* 977 (1924). A discussion of the merits of quinone for tanning wool and for mordanting.

165.—Physicochemical Contributions to the Theory of Mineral Mordanting of Animal Fibers.

Egon Elöd. *Kolloidchem. Biehefte 19,* 299-362 (1924). The first step in the mordanting of animal fibers is the hydrolysis of the mordant. The role of the liberated acid depends on its electrolytic dissociation. Weak acids (formic acid) are mainly adsorbed, but with mineral acids adsorption is followed by chemical reaction. Proof of the above is furnished by correlated acidimetric, potentiometric, and soluble protein determinations and by the decrease of the tensile strength of the fiber following the action of mineral acids. The decomposition of the fiber is unessential for the mordanting effect and can be eliminated by addition of sodium biformate. $Na_2Sn(HCO_2)_6.5H_2O$ is the only organic tin salt suitable for weighting. In the mordanting of wool with aluminum sodium biformate gives the best results, while potassium bitartrate does not sufficiently promote hydrolysis, owing to the formation of a stable complex aluminum tartrate.

166.—Physiochemical Contributions to the Theory of Mordanting. II.

E. Elöd. *Z. angew, Chem. 38,* 199-201 (1925). Mordanting for 8 to 14 days at 18° is required with alizarin to produce the same shade on wool as mordanting for 1 to 1.5 hours at 100°. Since the color intensity is proportional to the amount of aluminum hydroxide in the fiber, the deposition of aluminum hydroxide is a chemical process and is not due to adsorption, the rate of which decreases with rising temperature. The process is independent of the condition of the mordant as the same result was obtained with a solution prepared 14 days before use.

167.—Process for the Dyeing of Mordant Colors on Wool.

J. M. Matthews. *Chemicals 23,* No. 21, 151-3 (1925). This is a discussion of the chemical and colloidal theories of mordanting wool.

168.—Studies of Mordanting and Dyeing Phenomena. VIII.

E. Elöd and E. Silva. *Z. physik. Chem. Abt. A 137,* 142-75 (1928). Elöd and Silva consider single-bath chrome tanning of hides, tin weighting of silk, mineral mordanting of wool, and the acid dyestuff conditions to be very similar phenomena. In the systems investigated the conditions were found to be suitable for existence of Donnan membrane equilibrium. The acid-binding power of hide and wool with varying pH values agrees with Procter and Wilson's work and with Loeb's data for the swelling of gelatin. The action of acid dyestuffs on hide substance and wool depends on the taking up of dyestuff anions, which is influenced by the pH of the bath, added electrolytes and dyestuff concentration. The conditions for maximum uptake

of dyestuff from solution are calculated and agree with experimental results. Single-bath chrome tanning is due to the hydrolysis of the chromium salt and agrees exactly with the Donnan theory. In mineral mordanting of wool and tin weighting of silk there is a hydrolysis that is accelerated and increased by the membrane action of the organic materials.

169.—Primary Action of Chromic Acid on Wool Fiber.
M. A. Il'inskii and D. I. Kodner. *Z. angew. Chem. 41,* 283-5 (1928). Wool fiber absorbs chromic acid from solution, even in the presence of mineral acids, to form a complex in which the wool substance acts as a base, combining with about 10% of chromic acid. This is about the equivalent quantity on the assumption that the molecule contains two basic groups. The complex is stable towards water.

170.—Investigation of Tippy Dyeing on Raw Wool with Top Chrome Colors.
C. C. Westbrooke. *Textile Colorist 51,* 583-5 (1929). Dyeings with top chrome colors which were found to give tippy effects on raw Texas wool were made on several varieties of raw wool, on cloth exposed in the Fade-Ometer, cloth exposed to the weather, and unexposed cloth. The results indicate that tippy dyeing is due to the effect of light on wool and not to its processing prior to dyeing. That the effects of light and weather are identical is not proved conclusively, although the test results indicate that this is the case.

171.—The Behavior of Wool Fiber Toward Chromium Trioxide and Dichromates.
R. Haller and H. Vom Hove. *Helv. Chim. Acta 15,* 357-75 (1932). The adsorption of chromium trioxide and of potassium dichromate on wool fibers follows parabolic curves when potted against percentage in solution or against time. For the same percentage in solution and time, chromium trioxide is adsorbed in greater amounts than is potassium dichromate. Fibers so treated behave as follows as to the oxidizing influence of chromium compounds, determined by tests of strength and elongation: In sunlight, they are strongly attacked in air, slowly in dilute sulfuric acid; in the dark, these effects are retarded and require days or weeks in some cases. The accelerating effect of sulfuric acid is retarded by the addition of Glauber salt. The reduction of chromium trioxide under the influence of light and the deterioration of the wool fibers proceed approximately parallel to the adsorption. In these treatments sexivalent chromium is reduced first to chromic chromate and then to chromic oxide. Chemical changes in the wool are recognized by the presence of sulfate ions and by specific protein reactions.

See 212.

DYEING, Theory of.

172.—Theory of Dyeing.
L. Vignon. *Compt. rend. 112,* 623-624 (1891). The author concludes that dyeing with soluble dyes and textile fibres or metallic oxides is a process of a purely chemical order and depends essentially on the presence of basic and acidic functions in the coloring matter and its absorbent.

173.—Theory of Dyeing.
A. Binz and Georg Schroeter. *Ber. 35,* 4225-4229 (1902). The so-called "salt" theory of dyeing, which assumes that a salt is produced between the acid or basic dyes and the amino acids of the wool or silk, is shown in several cases to be untenable, since certain acid coloring matters will dye in the presence of an excess of sodium hydroxide, and some basic dyes in the presence of strong hydrochloric acid. Dyeing experiments are described with the following: Azobenzenesulphonic acids, p-hydroxyazobenzene, p-amino-azobenzene, p-dimethylaminoazobenzene, *m*:*m*'-diaminoazobenzene, and tetramethyl-*m*:*m*'-diaminoazobenzene.

174.—Theory of Dyeing Process.
G. Von Gorgievics. *Chem. Ztg. 26,* 129-131 (1902). This is an account, historical and critical, of the various papers published since 1894 on the theory of dyeing, which cannot be briefly abstracted.

175.—The Process of Dyeing.
A. Binz and G. Schroeter. *Ber. 36,* 3008-3014 (1903). It is suggested that the dyeing is due to salt-formation between the dye and the fibre and that the sulphonic acid is able to compete with a mineral acid for the basic radical of the fibre, while the feeble carboxylic acid is completely displaced by mineral acids. p-Hydroxy- and o-p-dihydroxy-azobenzenes, on the other hand, are absorbed in neutral, acid, and alkaline solutions, the absorption being only slightly reduced by excess of alkali when the latter is beginning to act on the wool. These are regarded as combining in the quinonoid form with the fiber, possibly forming an additive compound of the pinhydrone type.

176.—Bleaching and Dyeing.
E. Justin-Mueller. *Rev. gén. mat. col. 7,* 72 (1903). The dyeing of wool or silk by basic dyes depends on an addition reaction between the carboxyl groups of the fiber and the ammonium compounds, while the action of acid dyes is due to the addition reactions between radicals of the dye and the amino compound of the wool.

177.—Behavior of Wool Fiber to Certain Acid Dyes. Contribution to the Theory of Dyeing.
Edmund Knecht. *Ber. 37,* 3479-3484 (1904). Experiments made with orange G and crystal ponceau, ponceau 2G and xylidine ponceau, orange II and "fast" red A, "fast" acid fuchsin B, the corresponding naphthylamine dye, picric acid, *s*-trinitrocresol, and *s*-trinitroxylenol indicate that the amounts of dye taken up by the wool fiber are in the ratios of the molecular weights of the dyes. The amount of dye taken up does not vary much with the amount of water present. The actual amount taken up was determined by estimating the amount originally in the solution and then the amount left after dyeing. All estimations were made by the use of titanium trichloride. This method, however, did not yield good results with trinitrocresol and trinitroxylenol. In the case of crystal-ponceau, the curve representing the relationship between amount of dye (in per cent) present and amount taken up by the fibre is a straight line until 17 per cent has been absorbed, after which it rises rapidly and runs nearly parallel to the vertical ordinate.

178.—Silk and Wool as Dye Producers.
H. Pauly and A. Binz. *Z. Farb. Text.-Ind.,* 373-374 (1904). The authors think that the tyrosine which is in human nails and hair, and in silk and wool, is the cause of the dyeing of these substances when they are immersed in solutions of diazonium salts. The tyrosine ($HO.C_6H_3.CH_2.CH(NH_2).CO_2H$) as a phenol, gives rise to a hydroxyazo-compound. Histidine may behave in a similar way in the case of other physiological substances which interact with diazonium-salts. When *p*-phenylenedimethyldiamine is oxidized by bromine water in the presence of wool or silk, a dark gray dye is produced on the fibre; a dye of the same shade is formed by a similar oxidation of the same base in the presence of tyrosine. This fact probably shows that the latter substance is the source of a dye on the fibre, and that the latter is analogous to the dyes of the indophenol or oxazine series.

179.—Physicochemical Theory of Dyeing.
E. Lazuech. *Rev. gén. chim. 10,* 433-4 (1907). Considering dyeing as a case of solid solution, the dyestuff being dissolved in the fiber, the author points out several applications of the ionic theory in explaining the theory of dyeing. . . . Salts are added to the dye bath to increase the osmotic pressure of the liquid above that of the solid so that the dye is forced into the fiber. Dyes enter the fiber first in the ionc state, and when the limit of dissociation has been reached combine to form the

undissociated dye. For example, oxamine red M T dyes first a red-brown, the color of its ions; later, a violet-brown, because the blue color of the product adds itself to the color of the ions. Of two analogous dyes that one which is the better electrolyte is the better dye. The different behavior of different dyes during dyeing may be due to a difference in their osmotic pressure.

180.—The Influence of Acids and Bases on the Dyeing Process.
L. Pelet and N. Anderson. *Z. Chem. Ind. Kolloide 2,* 225-6 (1907). The authors determine the amount of dye fixed by 5 g of carefully cleaned wool when soaked five days in a solution of dye of known concentration, to which known amounts of acids or alkalies have been added. The acid or alkali in the solution is then neutralized and the dye remaining determined by colorimetry or titration. The results show that for solutions of crystal violet the wool adsorbs more dye the more acid the solution is, while in neutral solutions the adsorption is slight and in alkaline solutions almost nothing. With methylene blue the opposite is true, the adsorption being a minimum in acid solution and a maximum in alkaline solution. The constants of adsorption for fibers, charcoal, and silica are thus reliable only in neutral solution. The colloidal theory of dyeing explains this conduct. The acid bath charges the hydrogen ions of the wool positively and thus increases the fixation of the negative dye and hinders that of the positive dye, while an alkaline bath has the opposite effect.

181.—Gibb's Theory of Surface Concentration as a Basis of Adsorption, with an Application of the Theory of Dyeing.
C. M. Lewis. Liverpool Univ., *Phil. Mag. 15,* 499-526, April (1908). The results support the adsorption theory of dyeing.

182.—Dyeing and Adsorption.
L. Pelet-Jolivet. *Arch. sci. phys. nat. 25,* 430-52 (1908). This is a discussion including brief references to previous work connected with adsorption, (a) resume of our present knowledge on this subject, (b) methods of research, (c) tinctorial adsorption.

183.—Reactions Between Fibers and Dyes.
W. P. Dreaper and A. Wilson. *J. Soc. Chem. Ind. 28,* 57-60 (1909). The effect of dilute acids at various concentrations and temperatures was studied, as well as the reversibility of the effect of acids and the action of neutral salts. In general the condition of these dyes in the fibers could not be defined. The reversibility of the action indicates and equilibrium. With animal fibers the reactions are dependent on the concentration of acid and not on the ratio between the acid and dye on fiber.

184.—The Dyeing and "Felting" of Wool.
E. Justin-Mueller. *Z. Farben-Ind. 8,* 90-105 (1909). The author comes to the conclusion that it is possible to "felt" wool by heating in a bath of distilled water, without agitation, at a temperature slightly below 100°. The felting action may be increased by the addition of acids such as sulfuric and will increase in proportion to the amount of acid used. He further states that the felting action is more apparent when lime water is used than when distilled water is used, and the addition of a small percentage of sulfuric acid partially prevents the felting but larger quantities increase it. The author holds to his theory that continued boiling and the addition of larger quantities of acid bring the fiber into the condition of a gel. This is not requisite for the dyeing operation, as combed wool treated in a bath at a temperature slightly below 100° for one hour does not appear to felt and dyestuffs can be applied to the fiber by treating for only one hour under like conditions. It is well known that many acid dyes must be applied with the asssistance of an acid. The author explains this by saying that the acid brings the fiber into a condition approaching the gel. This applies to the ordinary dyeing operations to only a limited extent for two reasons: (1) the fiber is dye without traceable gelatinization ("felting"), and (2) gelatinization without the presence of acid is not sufficient for dyeing the fiber with certain dyes.

185.—Contribution to the Study of Dyeing. V.
V. L. Pelet-Jolivet and H. Seigrist. *Rev. gén. mat. color 13,* 252-4 (1909). Wool was treated with solutions, crystal ponceau, methylene blue, diamond fuchsin, sulfuric acid, potassium chloride, calcium chloride, aluminum chloride, barium chloride, and potassium hydroxide. The results are considered by the author to uphold his theory of electrification by contact and to be contrary to Justin-Mueller's theory that the diminution of the coefficient of solubility is of great importance in dyeing.

186.—Contribution to the Study of Dyeing. VI.
L. Pelet-Jolivet. *Rev. gén. mat. color. 13,* 254-8 (1909). A large number of experiments are described in which the heights to which various basic dyes, phthalic acid dyes, acid dyes, and direct cotton dyes ascended in strips of filter paper, linen, wool and silk were measured. A table is given which shows a correlation among the laws of electrification by contact, the laws of coagulation of colloids, the laws of dyeing, and the laws governing capillary ascension.

187.—The Nature of Wool and the Hydrolytic Processes Which Take Place in Dyeing.
W. Suida. *Z. angew. Chem. 22,* 2131-4 (1909). The keratin of wool is an albuminoid and readily undergoes hydrolysis whereby the wool becomes amphoteric. During the first period of hydrolysis there is a rapid increase in acid properties. These then diminish and the basic properties are retained to the end because the final products contain either guanidyl or imidazole groups. It seems probable that in dyeing, or mordanting, the acid or base combines directly with the basic or acid group of wool to form an insoluble salt. Wool is dyed by an aqueous solution of an acid dye, and in this case the basic groups of wool unite directly with the acid dye to form an insoluble salt. Wool is dyed intensively on being treated with the hydrochloride of a basic dye. In this case the hydrochloric acid of the dye salt probably combines with basic groups of wool and the dye itself combines with acid groups, although it must be remembered that a hydrolysis of the wool is taking place so that quite appreciable quantities of it pass into solution and unite with the hydrochloric acid of the dye salt.

188.—Electrical Theory of Dyeing.
W. W. H. Gee and W. Harrison. *Trans. Faraday Soc. 6,* 42-70 (1910). The electrical theory of dyeing is based on the fact that any two bodies placed in contact are oppositely electrified. It explains how one type of coloring matter is selected in preference to another by the fabric.

189.—Studies on the Causes of Coloration of Animal Fibers. II. The Power of Guanidine Derivatives to Precipitate Coloring Matter.
W. Suida. *Z. physiol. Chem. 68,* 381-90 (1910). The author here uses a new reagent to test the acidity or basicity of a number of dyes which (dissolved in water) with acids alone do not form precipitates. The reagent is prepared by dissolving 5 g of guanidine-hydrochloride and 3 g of acetic acid in 100 ml of water. The results may be thus summarized: No precipitates are formed with purely basic, nonsulfonated dyes. Dyes which are aminosulfonic acids generally show a decrease of precipitability with an increase in the number of amino and sulfo groups though the generalization is not absolutely reliable. Nearly all of the hydroxyazo dyes examined, with the exception of eosamine B

and azomagenta G, picric acid, and alizarin red, are more or less quantitatively precipitated. The degree of precipitation is controlled by the positions of the hydroxyl and the sulfo groups. The degree of precipitation of hydroxy dyes containing free or alkylated amino groups decreases with the increase in amino groups. Although tartrazine does not give a precipitate, dyes containing hydroxyl and carboxyl groups, or these and sulfo groups, give precipitates whether amino groups are present or not. But dyes which contain amino (or alkylated amino) and carboxyl groups but do not contain hydroxyl groups give no precipitates. From these experiments the important part played by phenolic hydroxyl and aromatic amino groups in the fixation of acid dyes by basic substances is shown. The influence of the carboxyl and sulfo groups is very subordinate and unimportant. Since phosphotungstic acid is an excellent precipitant for the basic decomposition products of proteins and since these products often contain the group nitrogen-carbon-nitrogen there can be little doubt that it is the nitrogen-carbon-nitrogen group contained in the proteins which causes the fixation of acid dyes. Also the chemical compounds formed by acid dyes with animal fibers are probably formed in stoichiometric proportions, since Radlberger has shown that compounds of guanidine with acid dyes are constituted in this way.

190.—Change in the Chemical Properties of Dyestuffs After Deposition on Animal Fibers.

W. Suida. *Chem.-Ztg. 36,* 622 (1912); *J. Soc. Chem. Ind. 31,* 584 (1912). The nitroanilines when deposited on wool cannot be diazotized and combined with azo dye components. *p*-Aminoazobenzene, *p*-aminoazotoluene, and dehydrothio-*p*-toluidine darken in color slightly on diazotization, but no combination with azo dye components can be effected, so that no true diazo compound is formed. If, on the contrary, the wool is first boiled with R-salt and then treated with nitrodiazobenzene, the coupling takes place readily with the production of a red color. It is therefore probable that the above bases are attached to the wool by means of their amino groups. Primuline, which contains a sulfoxy group, retains all its diazotizing and coupling properties on wool. This appears to suggest that in this case the amino group is free and that the sulfoxy group is the point of attachment between the fiber and the dye.

191.—Mechanism of the Acid Dye Bath.

M. Fort. *J. Soc. Dyers Colourists 29,* 269-77 (1913). The function of the assisting acid and sodium sulfate in dyeing wool with acid colors has been variously explained according to chemical laws (Hallitt, Ibid, 1899, 30). According to Fort the role of the acid, acting on the wool, is the development of the latent basicity of the wool, and that upon this increase in the available number of groups in wool substance depends the actual dyeing or combination of dye with fiber. The main difficulty in accepting the chemical theory of dyeing, as it has hitherto stood, is in the fact that the strong assisting acid (sulfuric) which is so readily taken up and tenaciously held by wool, would inhibit dyeing by preventing the dye acids from giving even the imperfect dyeings which they do when used alone on wool. Dyeing could proceed in such a case only by the displacement of the sulfuric acid already combined with basic wool substance by the dye acid. Local conditions in the fiber or in the immediate vicinity favor a reaction reverse to what takes place in the bath where the dye acid is displaced from combination with sodium by sulfuric acid. Dyeing with the sodium salt depends upon a double neutral salt reaction, while the dyeing with a free color acid is less complete and depends entirely upon one of the neutral salt reactions taking place in the first instance.

192.—The Theory of Dyeing.

W. D. Bancroft. *J. Phys. Chem. 18,* 1-25 (1914). This is a discussion of data in the literature.

193.—The Theory of Dyeing. II.

W. D. Bancroft. *J. Phys. Chem. 18,* 118-51 (1914). This is a discussion of data in the literature.

194.—Theory of Wool Dyeings.

I. K. Gebhard. *Z. angew. Chem. 27,* I, 297-307 (1914). Contrary to the views of Knecht, it is not the easily split off soluble colloidal products of wool which are most important in fixing dyes, but rather the insoluble amorphous products. The nature of the sulfur in wool is still undetermined. Basic dyeings depend upon the presence of the carboxyl group; if this is alkylated, wool loses all affinity for basic dyes. Acid dyeings are the result of the formation of an inner salt, involving both the carboxyl and the amino groups. If only one of these is rendered inactive, the affinity for acid dyes is merely decreased, while to remove the affinity for acid dyes entirely, it is necessary to render both groups inactive. Inner salt formation renders wool inactive toward acid dyes, as is shown by the action of methylenedisaliylic acid.

195.—The Sorption Theory, a New Theory of the Dyeing Process.

G. V. Georgievics. *Chem.-Ztg. 38,* 445-6 (1914). Studies on the behavior of acids toward wool have furnished a new conception of the dyeing process which harmonizes the contradictions which exist among the current theories, the chemical theory, Witt's solid solution theory, and the physical or adsorption theory. In very dilute solutions, substantive dyes and acids are distributed between fiber and solvent according to Henry's law, which shows that the process is one of true solution. Only at very high concentrations are chemical compounds formed. This dualistic process is termed sorption.

196.—Theory of Dyeing. V.

W. D. Bancroft. *J. Phys. Chem. 19,* 145-58 (1915); cf. the preceding abstract. This paper deals with fastness to soap and to light.

197.—The Mechanism of the Acid Dye Bath.

M. Fort and E. Pearson. *J. Soc. Dyers Colourists 31,* 222-4 (1915). A chemical reaction of the type: Wool basic hydrate-sulfuric acid + sodium salt of color acid = wool basic hydrate color salt + sodium sulfate has been claimed as the main feature of the absorption of an acid dye caused by the addition sulfuric acid to the dye bath. Experiments have not been conducted with a different acid (hydrochloric). Three 5-g samples of merino wool were treated (1) with 0.1 *N* hydrochloric acid, and (2) pure crystal scarlet, (3) similar amounts of hydrochloric acid and dye combined. The dye was completely absorbed in (3), what remained in (2) was estimated with titanous chloride and the hydrochloric acid in (1) and (3) was estimated by titration with 0.05 *N* sodium hydroxide. Similar experiments were conducted with Botany sliver and common flannel. From the results the following conclusions are drawn: (1) In the dyeing of wool with the sodium salt of crystal scarlet aided by hydrochloric acid, a chemical reaction takes place. As dye is being taken up by the wool, mineral acid (which takes precedence in absorption by fiber) is displaced from combination with the wool, which receives the color acid of the dye in its place, and the displaced mineral acid simultaneously unites with the sodium of the dyestuff. (2) In the dyeing of crystal scarlet color acid on wool from a sulfuric acid bath, a similar chemical reaction takes place to that described in (1) except that no bases other than those derived from wool are present. The mineral acid displaced from the combination with the fiber re-enters the bath in the free state apart from combination with basic matters provided by wool.

198.—Theory of the Acid Dye Bath.

M. Fort. *J. Soc. Dyers Colourists 32,* 33-

40 (1916). A theory has been constructed to explain the taking up of acid dyes by materials which are able to effect combinations with acids. Commercial dyeing with acid dyes is mainly dependent on the use of a free acid in conjunction with the dye. The aid thus rendered to the dyeing is dependent on the chemical reaction between dye and the acid fiber compound formed initially and not, as hitherto commonly supposed, on a process of liberation of free color acid in the bath.

199.—Theory of Dyeing.

P. Pfeiffer and F. Wittka. *Chem.-Ztg. 40,* 357 (1916); *J. Chem. Soc. 110,* I, 495. The authors' experiments with pure amino acids and polypeptides lend further support to the theory of Nietzki that the compounds of dyes with the silk or wool fiber are salts in which the amino acids or proteins function either as acids or bases. Magenta solution decolorized by the addition of ammonia assumes again its red color on the addition of glycine, glycylglycine, leucylglycine, etc., just as is the case on adding ammonium acetate. The added acid is distributed between the ammonia and the magenta base, with the formation of the magenta salt of the amino acid. On the other hand, salt formation occurs through the basic functions of the polypeptides, when a weak alcoholic solution of the quinonoid ethyl ester of tetrabromophenolphthalein becomes blue on the addition of glycine, etc., in the same way that the blue ammonium salt of the phenolphthalein derivative is produced on adding ammonium acetate to the above solution. The ability of polypeptides and also polyhydric alcohols to form molecular compounds with neutral salts may also acount for the action of substantive dyes both on silk and wool and on cotton.

200.—Physical Chemistry of Dyeing. Acid and Basic Dyes.

T. R. Briggs and A. W. Bull. *J. Phys. Chem. 26,* 845-75 (1922); *Am. Dyestuff Reptr. 11,* 447-50, 461-2; 12, 36-42 (1923). The chemical and physical (adsorption) theories of dyeing are briefly stated. The object of this study was to investigate the dyeing of wool with acid and with the basic dyes from the standpoint of the adsorption theory of dyeing as formulated by Pelet-Jolivet and Bancroft. The work was carried out rigidly, with control so far as possible of all the variables involved, but particularly the hydrogen-ion concentration of the dye bath. The effects of dyes on the adsorption of acids by wool and of acids on the adsorption of dyes were determined quantitatively for typical acid dyes. The taking up of dyes by wool is adsorption and the amount of dye adsorbed varies continuously with a change in the hydrogen-ion concentration of the dye bath. No evidence of chemical action between dyes and wool has been found. The hydrogen electrode was used throughout to determine the hydrogen-ion concentration of the exhausted dye bath and in some cases also in the titration of free residual acid. The action of assistants is strictly in accord with the theory.

201.—Reactions of Wool During Dyeing.

R. Haller. *Z. ges. Textil-Ind. 25,* 402-3, 411-2 (1922). Wool which has been treated with sodium plumbate reveals on examination with dark field illumination a non-uniform deposition of lead sulfide, which indicates that at least a part of the sulfur is present in the elementary state in a fine granular form. Microscopical examination of wool dyed both with substantive and with acid dyestuffs shows perfectly uniform distribution of the coloring matter. The use of substantive dyestuffs in dye-baths containing no electrolytes often results in practically none of the dyestuff being absorbed by wool. Treatment with sulfuric acid of wool dyed with basic dyestuffs shows that the greater part of the dyestuff is absorbed by the cortical layer, the epidermis being only slightly colored. Aqueous sodium hydrosulfite solutions are recommended for estimating the strength of dyeings. If a salt is formed by the combination of wool substance with rosaniline base, it is very readily decomposed. Wool dyed with mordant and vat dyestuffs shows perfectly homogeneous coloration under the microscope. The production of homogeneous dyeings on wool shows that the micelles are able to move apart in the same way as those of cotton. Wool is not dyed by ethereal solutions of malachite green base, but if such a solution is evaporated to dryness and the residue dissolved in alcohol, the solution is colored green and is capable of dyeing wool. If wool, which has been dyed with fuchsin and subsequently treated with alcohol until no more color is extracted, is dyed with malachite green or methylene blue, a considerable quantity of the dyestuff is absorbed. The evidence obtained by a series of experiments with ammoniacal solutions of fuchsin is opposed to the supposition that wool is amphoteric, a supposition which fails to explain the dyeing of jute and khaki cotton.

202.—Dyeing of Deaminated Wool.

W. W. Paddon. *J. Phys. Chem. 26,* 384-9 (1922). The experiments verify the work of Bentz and Farrell and furnish quantitative data regarding the dyeing of deaminated and of ordinary wool by the typical acid dyes orange II and lake scarlet R. The quantitative experiments show that amino groups in wool play no part in the dyeing of that fiber by acid dyes.

203.—Further Contributions to the Knowledge of Adsorption Compounds. IV.

R. Haller. *Kolloid. Z. 33,* 306-9 (1923). A study of the adsorption by cotton and wool of colloidal suspensions of dyes, such as indanthrene blue RS, indigo, alizarin VI, etc., with and without electrolytes. In every case the dyeing was more marked and the attraction between adsorbent and dye was more intense the greater the degree of dispersion of the pigment. Wool is a much better adsorbent than cotton. Wool forms lasting and stable "compounds" with substances that are doubtless quite inactive chemically; this must result from adsorption. The observations make it seem very questionable whether the dyeing of wool is a chemical process. In the first place many analogies exist with the process of dyeing cotton with substantive dyes, which has been recognized for a long time as an adsorption process. Moreover the pigment must possess a definite degree of dispersion in order to produce the maximum coloring. Finally, fibers are colored more intensely than a fabric prepared from the spun threads,—a result that must follow from the much greater adsorbing surface of a bundle of loose fibers.

204.—The Dyeing Process. I. The Absorption of Acid Wool Dyes of the Type—Orange II.

P. Ruggli and A. Fischli. *Helv. Chim. Acta 7,* 496-506 (1924). To test the theory that for the three simple cases of dyeing—acid dyes on wool, basic dyes on wool, and direct cotton dyes—the affinity of dye and fiber depends largely on the solubility of dye, the rapidity and completeness of dyeing by various dyes of the same structure but with different numbers and positions of sulfo groups were determined. 0.0002 mole of dye (as the sodium salt), 2.5 g of wool yarn and sufficent sulfuric acid to liberate the dye acid and create the desired excess (expressed as per cent by weight of the wool) were diluted with water to 100 ml at 100° with stirring, the yarn was extracted after a definite time and the remaining color determined by titration with titanous chloride. With 5 per cent excess sulfuric acid, the speed of dyeing was too great to measure accurately. With 1 per cent excess, the mono-sulfonic dyes were most rapidly absorbed, the di-sulfonic dyes next, etc., showing that the least soluble dyes (with the fewest acid groups) were most rapidly absorbed. But the sulfonic groups have a specific affinity for wool fibers as is shown by the fact that more dye is absorbed at equilibrium if more sulfonic groups are present, although the

mono-acid dyes are irregular. This is explained by the hypothesis that the relative insolubility (shown by too much being absorbed) in the excess acid bath masks the effect of the acid groups. This was supported by the results of dyeing without excess acid where the equilibria were found to be entirely regular.

205.—The Behaviour of Wool as an Amphoteric Colloid: A Contribution to the Theory of Dyeing.

J. B. Speakman. *J. Soc. Dyers Colourists 40,* 408-11 (1924). While four theories are still necessary to explain dyeing phenomena, data favoring the chemical theory for dyeing wool and silk with acid and basic dyes are given. The disfavor of the chemical theory of dyeing wool and silk appears to be largely due to the non-recognition of the fact, shown by Loeb, that as proteins they behave as amphoteric colloids. On the line of Loeb's investigations on the proteins, it is shown that the absorption of acids by wool follows the laws of ordinary chemical combination and not the empirical rule of adsorption as assumed by Georgievics. From data by Georgievics, Fort and Lloyd, Kohlrausch and Loomis, Noyes and Dietl, it is shown the amount of acid absorbed by wool is proportional to the hydrogen-ion normality of the solution remaining after the absorption is complete. Orthophosphoric acid acts in this case as a monobasic acid and sulfuric acid in part as a monobasic acid, more so as the concentration increases. Oxalic acid behaves as a monobasic acid over most of the range studied. These results agree with the theory of chemical combination within the limits of experimental errors. This shows why one acid is absorbed more than another and if the acids are placed in the order of increasing absorption for the same hydrogen-ion concentration, a perfectly intelligible result is obtained. It is therefore evident that the absorption process in this case is of a chemical nature, and it is more than probable that the dyeing of silk and wool with acid and basic dyes is due to chemical forces and changes. The data are presented in graphs and tables.

206.—The Relation Between the Nitrogen of Wool and Its Affinity for Acid and Basic Dyes.

E. R. Trotman. *J. Soc. Dyers Colourists 40,* 77-9 (1924). A review of previous work is followed by the results of dyeing experiments on deaminated as compared with ordinary wool. These experiments show that except in the case of fast red, the deaminated wool had the same affinity for acid dyes as ordinary wool. The conclusion is that the primary amino group does not assist in dyeing wool with acid dyes. Wool treated with cold nitrous acid, followed by boiling, has an increased affinity for basic dyes, probably by conversion of amino groups into carboxyl groups.

207.—Theory of Dyeing.

E. Elöd. *Textilber. 6,* 742-3 (1925). The quantitative absorption of dye by wool is independent of the pH of the bath. The isoelectric point of wool cannot be exactly defined as it is the resultant of the isoelectric points of several substances, the relative proportions of which vary considerably with the wool and its previous processing.

208.—The Theory of Dyeing Processes.

E. Elöd. *Festschrift 100-jahr* Besteh. Tech. Hochschule Karlsruhe 1925, 490-6; *Chem. Zentr.* 1926, II, 2632-3. From the point of view that both physical and chemical processes play a mutually important role in dyeing, the dyeing of wool with acid and basic dyes was investigated. Special attention was directed to the part played by the pH value of the bath during the dyeing. The action of crystal violet on wool results in an increase in the pH value of the bath after the dyeing, because of liberation of hydrogen ions from the wool into the solution. This is independent of the concentration of the dye or of the quantity of the dye taken up by the wool. The initial value of pH depends upon the initial concentration of the dye, while the final value of pH is independent of both the concentration of the dye and of the quantity of wool. Contrary to the data of Briggs and Bull, the quantity of dye taken up from solution by the wool does not depend directly upon the pH value of the bath. With acid dyes the alkalinity of the bath is greater after the dyeing, but here too there is no relationship with the quantity of dye absorbed. Measurements of pH during the action of acid and of alkali solutions on the same kind of wool showed that wool absorbs hydrogen ions from solutions which are more acid than pH 4.6, whereas the wool liberates hydrogen ions in solutions having a pH value over 4.6, with accompanying decomposition of the wool substance. At pH 4.6 the hydrogen-ion concentration does not change on account of reactions between the wool and the solution, and at this pH the wool is not decomposed. The analogy between this phenomenon and the behavior of amphoteric electrolytes at the isoelectric point allows the assumption that the value of pH 4.6 is a mean value for the isoelectric points of several amphoteric substances comprising the wool substance of the particular grades of wool examined. In any case the wool with its wool substance takes an active part in the dyeing process and does not behave as an adsorbent in the classic meaning of the term, which involves reversibility, and therefore a purely physical conception of the dyeing process appears to be inadequate.

209.—Theories of Dyeing.

S. H. Jenkins. *Dyer 55,* 152-3 (1926). While the author appears to favor the chemical theory for dyeing silk and wool "the complexity of dyeing phenomena indicates that none of the theories can alone adequately explain the numerous facts that are known. Experiment has shown that chemical, physical and physico-chemical action may take place, and therefore it is only by a combination of the theories that a satisfactory explanation may be attempted."

210.—Chemistry and Physics of Dyeing. III. Dyeing Wool with Acid Colors.

K. M. Meyer and H. Fikentscher. *Melliand Textilber. 7,* 605-10 (1926). Wool, which according to x-ray studies possesses no crystallite character like that of cotton, reacts with acids like any other albuminoid to form salts. Regardless of the fineness of the wool used, and consequent total fiber surface, 100 g of wool react with 0.08 gram equivalent of any acid. This indicates that about 1/13 of the nitrogen in wool, or 1.1 per cent, is basic. Of the basic nitrogen, the van Slyke reaction shows that about one-third is in the form of primary amine, and it was found that even most careful deaminization failed to remove all of the basicity of wool. Hence some of the basic groups of wool are weaker than others. With weak acids, or color acids, a large excess of acid is necessary to repress the hydrolysis of wool salt, which follows the Ostwald dilution law. A practical consequence is that in dyeing operations the wool basicity is rarely completely utilized.

211.—Theories of Dyeing.

A. P. Sachs. *Textile Colorist 49,* 15-7, 238-42, 312-4, 385-8, 529-33, 603-5, 669-70 (1927). This presents a general review of the theories of dyeing in which stress is laid on modern physicochemical and colloid-chemical data relating both to the dyestuff and the fiber.

212.—Studies of Mordanting and Dyeing Phenomena. VI. and VII.

Egon Elöd and E. Pieper. *Z. angew. Chem. 41,* 16-9 (1928). Wool and silk, being amphoteric, tend to reach their isoelectric points when warmed in alkaline or acid solutions. Thus, the presence of basic or acid dyes does not affect the final pH. With wool the basic dye taken up increases with increase of pH up to 10; above this there is a decrease due to an increase (observed ultramicroscopically) in

the size of dye particles, without influencing the nature of the change in pH value. With an acid dye the maximum amount is taken up at a pH of 2, above which there is a decrease due to increase in size of dye particles. The curve showing the relation between dye absorbed and final pH value is continuous, there being no break at the isoelectric point; this indicates that the taking up of dye by wool or silk is due not entirely to the formation of protein salts.

213.—Chemistry of the Dye Bath. Theories of Yesterday and Today.

P. E. King. *Times, Trade and Eng. Supplement (London) 23,* 44 (1938). Wool, silk, and cotton are negatively charged when placed in water, as are also certain classes of dyestuffs. Wool in an acid liquor is positively charged, as are basic dyestuffs. The modern tendency is to regard dyeing phenomena as resulting from more than one factor, e. g., chemical adsorption and electrical actions may occur.

214.—Theories of Dyeing Wool.

A. P. Sachs. *Bull. Natl. Assoc. Wool Manufrs. 57,* 243-51 (1927); *Dyetuffs 29,* 1-6 (1928). The various theories are discussed. The reaction between wool and dyetuff is probably similar in general nature to, but different greatly in detail from the reaction between other textile fibers and dyestuffs. The process of dyeing wool is strictly a colloid-chemical phenomenon, involving adsorption of the dyestuff by the fiber, due to differences in electrical potential and the formation of a chemical compound (a salt of wool and dyestuff), which causes the dyeing to be fast and prevents the reversal of the adsorption. The colloid-chemical theory of dyeing wool reconciles the facts previously observed which formed the basis of rival and mutually contradictory theories of dyeing.

215.—Mistaken Ideas on the Properties of Wool.

Haller. *Boll Assoc. ital. chim. tessili color. 6,* 77-9 (1930). The acid group of wool does not combine with the basic group of the color bases. The belief is incorrect that an acid should be added to the dye baths with acid colors to liberate the coloring acid so it can combine with the basic group of wool and form a salt of the color, as a 1% crystal ponceau water solution, despite prolonged boiling, dyes wool only slightly; it requires the addition of acid for normal dyeing. On the other hand, fast orange O dyes wool well in a neutral or an acid bath. The barium salt of fast orange O is fixed on wool as a color salt. With methylene green a very weak reducing action is obtained. Wool absorbs a small quantity of potassium dichromate which is not eliminated by washing and not reduced to chromic acid.

216.—Theory of the Dyeing Process (Model Experiments).

P. Pfeiffer, O. Angern. Liu Wang, R. Seydel and K. Quehl. *J. prakt. Chem. 126,* 97-145 (1930). The functional building units of wool and silk, the amino acids and acid amides, have a pronounced affinity for dyes of various kinds, with which they form well-characterized addition products in stoichiometric relations. The auxochrome groups (NH_2,HO,CO_2H and SO_3H) are the active agents in the formation of these addition compounds, while the chromophore groups have no affinity for amino acids or acid amides. Hydroxyl and amino groups in the *o*-position to the chromophore group have little or no tendency to form addition compounds. The addition compounds show all the degrees of stability from loose molecular compounds to stable compounds of salt-like character. These results indicate that in the dyeing of wool and silk chemical forces must play an essential role.

217.—Heat of Combustion of Acid-Treated Wool and Its Relation to the Theory of Dyeing.

W. Passler and W. Konig. *Z. angew. chem. 44,* 288-91, 304-9 (1931). The modern theory of dyeing, with its adsorption features emphasized and with no requirements of chemical combination between the fiber and the dyestuff, apparently has to be set aside in certain cases where acid-reacting substances or dyes are combined with the animal fibers (wool and silk). There is a strong indication of some form of chemical combination taking place between the protein groups of the fiber substance and the dyestuff or certain dye intermediates. This proposition has been rather definitely established by determinations of the heats of combination between the fiber and the dye product (as shown by Vignon and others). The variation from the general physical theory is now supported by determinations of the heats of combustion of products obtained by the treatment of wool with various acids and acid-bearing dye-products. Thermochemical methods of study in this connection have been used by Vignon and Meyer, being based on the heat developed by the acidification of the fibers. The heat of combustion, as now determined for the acid-treated wool, was obtained by the use of a Huggershoff calorimeter. The results obtained are about 2 per cent lower than the previous work of Stohmann, which is rather close agreement in view of the indefinite character of the material used.

218.—Theory of the Dyeing Process.

A. E. Porai-Koshitz, A. Efimov, I. Shapiro, I. Riskin, N. Gorelik, M. Peskin, E. Veller, N. Sokolova and E. Vasil'eva. *J. prakt. Chem. 137,* 179-215 (1933). The mechanism of dyeing with substantive acid (cotton) dyes is investigated by using a neutral dye bath of the ammonium salt of the dye and determining the ammonia set free. Wool has a weak affinity for ammonia, which is removed by boiling in water. When wool is dyed in such a dye bath at the boiling point, ammonia is evolved in proportion to the dye absorbed (allowance being made for the affinity of the wool for ammonia). With cotton, however, the dye is absorbed as a whole and no ammonia is evolved. No appreciable dyeing occurs when wool is boiled in a neutral solution of the sodium salt of the dye, but in the presence of ammonium salts, dyeing takes place with the evolution of ammonia. The effect is not one of "salting out" as in the case of cotton, for whereas sodium sulfate and ammonium chloride have an equal effect in dyeing cotton, only the latter is readily effective in the case of wool. As ammonium salts do not precipitate the dye acids, this new technic makes it possible to use on wool substantive dyes that previously were considered unsuitable. The saturation value of wool for acid dyes is a stoichiometric relationship independent of the nature of the dye and is equal to the value for mineral acids (hydrochloric, sulfuric). Wool saturated with sulfuric acid from a 0.25 N solution takes up dye (chicago blue 6B) equivalent to the sulfuric acid present. Mutual replacement of dyes can occur when dyed wool is immersed in a solution of different dye (ammonium salt); if the wool is saturated, no ammonia is evolved. Conclusion: Whereas cotton dyeing is a purely physical process of adsorption, the dyeing of wool is a chemical process arising from combination of the dye acid with the basic wool fiber. An explanation is offered of the anomalous behavior of alkali blue, which is taken up by wool from weakly alkaline baths, but then gives dull, weak shades which develop into blue on addition of acids. It is shown that the behavior of wool free from volatile bases with the ammonium salt of the dye is normal and that the anion alone enters the fiber. It is suggested that in presence of alkali it does so in the carbinol form, which is dehydrated to the colored quinonoid form by acids.

219.—The Process of Dyeing Fibrous Materials. V. The Interaction of Animal Tissues and Ammonia Solution.

A. E. Porai-Koshitz. *J. Applied Chem.*

U.S.S.R. 99-102, (1934). In the boiling of wool and silk with ammonium chloride solution only hydrochloric acid is adsorbed by the material from the vat, and ammonia distills off. The amount of adsorbed hydrochloric acid is increased with increase in the amount of ammonium chloride in the vat solution. However, with 600 per cent of ammonium chloride for wool and 200 per cent for silk, the saturation limit is reached. This saturation limit is the same for wool as for dye anions, *i. e.*, 0.00083 g. equivalent per g of fiber, but for silk it is 1½ times higher than normal, *i. e.*, 0.0003 g equivalent per g fiber. This may be explained by the hydrolysis of the peptide groups of the silk. VI. Dyeing Wool and Cotton with Substantive Dyes of a Basic Character. *Ibid.* 103-12. Two tetra-azo dyes were synthesized from *m*-phenylenediamine with bianisidine and with *p,p'*-diaminodibenzylidene acetone. Over 90 per cent of the anions remain in the vats after the complete decoloration of the solutions, in dyeing wool with these dyes. From this it is concluded that wool absorbs only the cations of the basic substantive dye.

220. The Theory and Practice of the Dyeing Process.

A. E. Porai-Koshitz, E. A. Veller, N. V. Sokolova and E. Tz. Shukevich-Ershova. *Trans. Leningrad Chem.-Tech. Inst. U.S.S.R. 1,* 157-71 (1934). In the dyeing of wool and silk with eosin only the acid dye is absorbed by the fibers; the sodium hydroxide base remains in the bath. If ammonium salts are added then during the boiling an amount of ammonia gas is liberated corresponding to the amount of dye taken up. The "saturation capacity" of wool for eosin is 0.0008 g equivalent of dye per g of air-dried wool; of silk 0.00029 g equivalent—the same values as for sulfur dyes. In dyeing, eosin acts as a dibasic acid. Addition of ammonium salts hastens the dyeing process and gives a more evenly dyed product.

221.—A Contribution to the Chemical Theory of Dyeing; The Affinity of Deaminated Wool for Acid Dyes.

J. B. Speakman and E. Stott. *J. Soc. Dyers Colourists 50,* 341-8 (1934). This is an investigation purporting to determine the conditions necessary for complete deamination of wool and to study the affinity of the deaminated wool for acid dyes. It is concluded that wool does not combine with acid solely through simple amino groups, and it is very difficult to deaminate wool completely. The guanidine group of arginine, the main basic amino acid of wool, reacts extremely slowly with nitrous acid and drastic treatment is necessary to insure complete reaction. When deaminated under these conditions, the affinity of deaminated wool for acid dyes is far less than that of untreated wool, and the main objection to the chemical theory of dyeing is removed.

222.—Mordanting and Dyeing Process. XXV. The Dyeing of Wool.

E. Elöd and N. Balla. *Melliand Textilber. 16,* 291-2, 323-4, (1935). Wool fibers were stretched 65 to 70 per cent in a 5 per cent soap solution at 50 to 55° and then dyed with direct dyes. Loose wool was treated in the same way but was not stretched. The stretched fibers took up about twice as much as the unstretched wool. There is no such difference with acid dyes. According to Elöd's conception of the structure of wool, the stretching breaks up the secondary valences of the wool and makes these available for direct dyes. The equivalent weight of wool is lower than that of silk; therefore wool takes up more from acid dyes than does silk. From direct dyes, on the other hand, silk, owing to its greater swelling capacity, takes up more than wool. Experiments carried out with diamine blue FF at 50° at pH 0.5 to 4.0 showed that wool takes up only very little from this, while silk under identical conditions takes up 33.0 to 12.0 mg of dye per g of silk. With decreasing pH values wool takes up increasing amounts of direct dyes without, however, showing the maximum observed with acid dyes. Wool dyed with direct dyes is faster than silk dyed in the same way. The addition of electrolytes decreases the amount of direct dyes taken up by wool. The reaction velocity of the dyeing process with acid is higher for silk than for wool.

223.—Principles of Dyeing with Acid Dyes.

L. R. Parks and P. G. Bartlett. *Am. Dyestuff Reptr. 24,* 476-8, 495 (1935). Dyeing with acid dyes is an adsorption phenomenon. Experimental data show that the behavior of acid dyes toward adsorbents is similar to the behavior of hydrochloric and nitric acids toward charcoal. The effect of inorganic salts on the adsorption of acid dyes is shown in tables. The acid character of acid dyes is shown to be due to the presence of hydroxyl groups, sulfonic acid groups, or carboxyl groups within the molecule, which ionize in water to produce hydrogen ions. The amount of acid dye adsorbed can be decreased by decreasing the concentration of either the color anion or the hydrogen ion. Increasing the pH in the dye bath by the addition of hydrochloric acid increases the amount of dye taken up by the adsorbent.

224.—Principles of Dyeing with Basic Dyes.

L. R. Parks and P. G. Bartlett. *Am. Dyestuff Reptr. 24,* 529, 536 (1935). The behavior of dye bases toward adsorbents is similar to that of sodium or potassium hydroxide toward charcoal. The amount of dye adsorbed depends on the pH of the bath. Experimental procedure and results are indicated.

225.—New Discoveries Relating to the Theory and Practice of Wool Dyeing.

L. P. Rendell and H. A. Thomas. *J. Soc. Dyers Colourists 51,* 157-72 (1935). An extensive set of tests permits the following conclusions: (1) During the dyeing of wool with all classes of dyes, turbulent conditions of the dye liquor promote much more rapid and complete penetration of the material and exhaustion of the liquor than do quiescent conditions. (2) With most acid and chrome dyes and many direct dyes, superior penetration of thick wool material and exhaustion of the dye liquor occur at 80° with turbulence of the liquor promoted by air bubbling or vigorous ebullition at diminished pressure as compared with ordinary methods. (3) With vat dyes, superior penetration of material and a stronger shade result from dyeing in a turbulent liquor at, below, or above the normally recommended temperature. (4) The physical condition of wool as regards tensile strength and cuticular damage after dyeing at 80° in a liquor into which air is bubbled and which is boiled vigorously at diminished pressures is superior to that of wool dyed at the normal boil. (5) The main causes of the simultaneously increased rate of exhaustion and penetration appear to be differential hydraulic and hydrodynamic pressures on either side of the fabric, whereby a reciprocating pump action of dye liquor through a fabric is induced and the vibrations or pulsations of the turbulent liquor which promote dyeing of the fibers. (6) Contributory causes of beneficial dyeing results are good circulation of the liquor and, with most dyes, an improved physical condition and stability of the dye liquor and a local concentration of dye at the air-liquid interface. (7) The application of air-bubbling in the manner described is a powerful aid to exhaustion and penetration and must be controlled to give strictly level shades. Ideal conditions are a uniform bombardment over the whole surface of the fabric in such a manner that the direction of the pressure gradient through the felt is being continually reversed.

226.—Acid Wool Dyeing. XXVIII.

E. Elöd and A. Köhnlein. *Melliand Textilber. 17,* 409-12 (1936). Graphs show

that in dyeing crystal ponceau (*I*) at 50° and at 20° the pH value (1.50) of the dye bath quickly rises to a maximum and remains at that maximum. The pH value at first increases but soon starts to decrease, and this decrease is proportional to the g of dye absorbed on the wool. To check this, samples of wool were treated with solutions of hydrochloric acid of pH 1.70 and pH 1.62 and wrung out. The solutions after treatment were pH 2.00 and 1.87. Samples were then dyed in baths of varying concentrations from 1 to 4 per cent and the pH was increased from 2.11 to 2.29; the pH decreased from 1.71 to 1.40 and the g *I* per 100 g wool increased 12.45 to 14.00 respectively. Other graphs show that the speed of dyestuff absorption is dependent on the pH of the dye bath, the optimum pH for *I* being 1.23. Graphs also illustrated that for definite pH values, 1.0 to 2.0, the amount of *I* absorbed by wool is almost independent of the dilution of the dye bath which in each case contained 1 g of *I*. One-g samples of wool were dyed at 50° for 4 hours with 0.2 per cent of *I* at pH 2.0 and the wool took 13.7 g *I* per 100 g wool. The same wool dyed a second time at pH 1.3 took up another 4.9 g dye. Another sample dyed like the first but at pH 1.3 took up 18.1 g *I*, showing that the amount of dye taken up by the wool depends on the pH of the solution.

227.—The Fastness of Wool Dyeings to Wet Treatments, II.

F. L. Goodall. *J. Soc. Dyers Colourists 52,* 211-18 (1936). The initial pH, above which the tendency for all acid dyes to be removed from wool is greatly increased, is 8.0 to 8.2. The effect is due to the alkali swelling effect of the fiber which is known to become significant at about this pH value. The nature of the extracting solution plays a very important part in the removal of dye from dyed wool by treatment with aqueous solutions. Aggregating or dispersing solutions produce respectively less or more removal of dye with colloidally dispersed dyes, but the aggregating or dispersing nature of the solution is relatively insignificant in the removal of molecularly dispersed dyes.

228.—Dyeing Phenomena in Wool.

R. Haller. *Helv. Chim. Acta 19,* 15-22 (1936). Wool was broken down into its histological elements by long-time treatment with cold concentrated ammonia solution. The dissolved substance contains no tyrosine and no sulfur, adsorbs iodine strongly, and is colored by ammoniacal fuchsin, which also stains the cortex cells but not the epithelium. The epithelium is permeable to certain colloidally dispersed substances and yet impermeable to molecularly dispersed solutions of diazotized sulfanilic acid. Cotton red 10B in the cold or on short boiling hardly tints wool, but boiling for 10 minutes produces a strong coloration which under the microscope is shown to be entirely in the cortex while the intact epithelium is uncolored.

229.—Theory of Dyeing Animal Fibers.

A. E. Porai-Koshitz. *J. Soc. Dyers Colourists 52,* 19 (1936). A brief review of investigations by Porai-Koshitz and his collaborators to clarify certain misconceptions as the experimental methods in determining the nature of the changes which occur when wool and silk are boiled in solutions containing ammonium chloride and acid and substantive dyes in the form of sodium salts. The amount of ammonia liberated in a dye bath containing ammonium chloride and the sodium salt of an acid or a substantive dye is unaffected by the interaction between ammonium chloride and wool. The ammonia set free is exactly equivalent to the amount of dye-acid fixed on the fiber. Experimental data support the view that the dyeing of animal fibers with these dyes is a process of formation of definite salts from the fiber as base and the dye as acid.

230.—The Structure of Animal Fibers in Relation to Acid Dyeing.

J. B. Speakman. *J. Soc. Dyers Colourists 52,* 121-35 (1936). An attempt was made to determine how far structural differences between fibers and variations in fine structure brought about by change of pH and rise of temperature influence the rate of combination of animal fibers with acid dyes. The amount of dye absorbed by animal fibers from the circulating dye bath is a linear function of $\sqrt{t}$, despite the falling concentration of dye, because dye absorption takes place by diffusion from a film of approximately constant concentration on the surface of the fibers. The scale structure of animal fibers offers considerable resistance to the penetration of dye molecules, so that descaled fibers and fibers cut to short lengths show an increased rate of absorption over normal fibers. Differences between the rates of absorption of dye by the same weight of different animal fibers are determined mainly by variations in fiber diameter. At low temperatures all animal fibers offer considerable resistance to dye penetration, owing to the compactness of the micelle structure. The temperature at which successful dyeing can be carried out is an inverse function of the degree of dispersion of the dye.

231.—The Mechanism of the Acid Dyeing of Wool.

Hugo Vom Hove. *Z. ges. Textil.-Ind. Klepzig's 39,* 332-4 (1936). Dyeing experiments with naphthochromazurin B and cyano extra were made on untreated wool and on wool which had been boiled with acid and then freed from all salts by neutralization and dialysis. A dye lake which could not penetrate through the normal wool fiber penetrated deeply into the fiber which had been boiled with an acid. Thus, in ordinary dyeing operations the dye enters only a very small part of the exterior scale (even at the boiling point). If the outer layer is removed, as in the case of chlorinated wool, the dyeing can be completed in a much shorter time. A similar effect is produced by the oxidizing action of hydrogen peroxide and mechanically by Sieber's reaction, in which cut surfaces of the fiber and damaged spots are dyed by benzopurpurin 10B in the absence of acids, while the other portions of the fiber remain colorless. Gelatin exhibits an absorbing power for dyes on the wool fiber when it is used as an addition to the neutral dye bath. Many fast acid wool dyes exist as flakes in the acid dye bath as the dye acid is difficultly soluble. A change in these conditions occurs immediately when a soluble or highly swelling protein as gelatin comes into contact with the dye acid. A buffering action is produced, which raises the pH and thus increases the solubility of the dye or decreases the particle size, owing to the protective colloidal action of the protein. In both cases the penetration of the dye into the interior of the fiber is made possible. Wool that has been "closed" by means of tanning agents is not dyed under the normal conditions. Thus phenols exerted a protein protective effect in the hot acid bath.

See 8, 81, 82, 101, 161, 162, 261, 290, 295, 301, 302, 303, 311, 319, 324, 374.

ELASTIC CHARACTERISTICS.

See 222, 253, 260, 296, 320, 334, 336, 343, 361, 362, 365, 367, 368, 373, 374, 375, 378.

ELECTROKINETIC PROPERTIES.

232.—The Contact Potential of Textile Fibers in Water.

P. Karrer and P. Schubert. *Helv. Chim. Acto 11,* 221-9 (1928). The potentials at the surface of contact of a number of textile fibers in water have been determined. The experimental method and data are given. Wool assumes, in water, a strongly negative character.

233.—Electrokinetic Potentials, I. Measurements of the Electrokinetic Potentials at the Interfaces Between Fibers and Water.

N. Ando and A. Ando. *J. Chem. Soc. Japan 55,* 968-78 (1934). The electrokinetic potentials of cotton, silk, and wool were measured by the streaming-potential method. They were negative.

ENZYMES (See bacteria, etc.).
Also 136, 357, 358.

FELTING (See fulling).

FIBERS, Determination of, in Mixtures.

234.—The Quantitative Determination of Wool in the Presence of Cotton.

B. Ruszkowski and E. Schmidt. *Chem.-Ztg. 33,* 949-50 (1909). Wool contains 14 per cent nitrogen and cotton none. The process, which appears to give accurate results, consists in determining nitrogen by the Kjeldahl method.

235.—Notes on the Identification of Fibers of Animal and Vegetable Origin.

W. P. Dreaper. *J. Soc. Dyers Colourists 29,* 78-9 (1913). This deals with the detection of silk, cotton, and wool in admixture. But one solution is used; 2 g lead acetate dissolved in 50 ml distilled water to which are added 2 g sodium hydroxide dissolved in 30 ml water. The solution is boiled until clear, 3 g of magenta in 5 ml of alcohol is added after the solution has cooled to about 60°, and the volume is made up to 100 ml. A portion of the fabric is heated in this solution for 2 minutes to about a boil, then washed and placed in a dilute solution of acetic or formic acid and heated to 70°. Examined under microscope, silk will be dyed red, wool black or dark brown, and vegetable fibers remain uncolored. A solution of litharge in sodium hydroxide may take the place of the lead acetate, and picric acid may be substituted for magenta, in which case the silk will be dyed yellow.

236.—Morphology of Some Textile Fibers with Their Dry Distillation.

E. Beutel. *Kunststoffe 3,* 183-6 (1913). Photomicrographs. Method of distillation: The fibers are placed between two cover glasses (quartz or glass), held in a clip, and heated at one point near the edge with a micro-burner. The quartz glasses are 0.5 mm thick and 10 mm in diameter. The main differences between animal and vegetable fibers are: (1) Animal fibers soften on heating and melt; the plant fibers remain rigid. (2) Animal fibers increase significantly in diameter; plant fibers decrease. (3) The gas evolved together with expansion of the air produces characteristic vesicular formations in the refractory material left in the dry distillation of animal fibers; these are not observed on heating plant fibers. (4) Animal fibers melt together (coalesce) at intersecting or cross points and form vesicular masses; the cross position of plant fibers remain sharp. (5) Animal fibers yield a coke that adheres to the cover glass; the coke from plant fibers is easily removed. Wools, cottons, loaded and unloaded silks from different sources, Chardonnet silk, viscose silk, etc. were studied. The possibility of distinguishing natural from artificial silks, and these from one another, by the dry distillation test is pointed out.

237.—Quantitative Determination of Wool and Silk in Mixtures.

V. Villavechia and A. Capelli. *Rev. gen. mat. color 17,* 33-7 (1913). A comparison of methods.

238.—Test for Wool.

H. Leb. Gray. *J. Ind. Eng. Chem. 10,* 633-4 (1918). The fibers are placed on a microscope slide and covered with two drops of a 30 per cent solution of sodium hydroxide. The slide is then heated to boiling and immediately examined under the microscope. Wool fibers become swollen and some times dissolved; cotton and wood-pulp fibers remain unchanged except that they become clearer and slightly shrunk.

239.—Analysis of Mixed Wool and Cotton Fabrics.

Duyk. *Ann. chim. anal. chim. app. 2,* 324-30 (1920). Duyk recommends the following: Cut up 10 to 15 g of the material and dry at 100° to 105°, treat with appropriate reagents to remove size, filling material, etc., wash, dry, and weigh. Then heat with 2 per cent sodium hydroxide solution in a covered vessel on the water bath to a maximum temperature of 90° and continue the heating at this temperature for 20 minutes; remove the cotton residue, wash it with water, then with acidified water, and finally with water, and dry at 100° to constant weight. Then calculate the amounts of cotton and wool on the basis of the official limits for moisture, *viz.*, 17 per cent for carded wool, 18.5 per cent for combed wool, 8.5 per cent for cotton, and 10 per cent for silk. For the separation of silk from wool, boil the sample two minutes with zinc chloride solution (density 1.65).

240.—Analysis of Mixtures of Wool and Vegetable Fibers.

P. Krais and K. Biltz. *Text.-Forsch. 2,* 24 (1920); *Chem.-Ztg. 44,* Rep., 164. Fiber mixtures containing artificial silk cannot be analyzed by treatment with sodium hydroxide, since viscose silk loses 7 per cent and cuprammonium silk 6 per cent in weight. The artificial silk can be dissolved by treating 0.2 to 0.5 g of the mixture twice for one-half hour with 10 ml of a 1 per cent solution of ammoniacal copper oxide, (specific gravity 0.925), prepared by passing air for 2 to 3 days through copper turnings covered with a solution (specific gravity 0.905) of ammonia. The undissolved wool is then washed once with a concentrated solution of ammonia, once with a 10 per cent solution of ammonia, three times with water, treated for one hour with 10 per cent hydrochloric acid, washed with cold and then with hot water till neutral, dried at 110°, and weighed. Wool so treated loses about 0.42 per cent of its weight.

241.—Separating Wool from Other Fibers.

S. A. Ogden. *British Patent 214,963,* April 24, 1923. Fabric which may contain both wool and cotton is rapidly passed through sulfuric acid of 50° Bé at a temperature of 65°. The cotton is rapidly dissolved and the solution tends to form a coating on the wool fibers which protects them from the action of the acid. The wool is then quickly washed to prevent damage. If the proportion of cotton or other cellulosic fiber in the original material is small, the wool in the material may be given a preliminary coating to protect it from injury by the acid by dipping it in a thin cellulose paste.

242.—(Analysis of) Wool and Cotton Unions.

C. F. Green. *Textile Colorist 47,* 311-2 (1925). A discussion of methods of determining cotton or wool in unions.

243.—Improving Alkali Test for Cotton-Wool Mixtures.

A. F. Hedrick. *Textile World 67,* 3725-9 (1925). The method recommended is to condition a 2 g sample for two hours or more at 21° and 65 per cent relative humidity, and weigh. Boil moderately in about 100 times its weight of 5 per cent sodium hydroxide for one hour in a 400 ml assay flask with a reflux condenser. Filter through wire cloth, wash with water, then with 3 per cent acetic acid, and finally with hot water. Dry at 45 to 50° for 20 minutes, let stand overnight in the open air and condition at 21° and 65 per cent humidity as before. Results check to plus 0.3 per cent on duplicate samples, and should be corrected by 5.6 per cent for loss of cotton.

244.—Destroying Silk in a Mixture of Silk and Wool.

D. C. Chisholm and J. A. Hannum (to George E. Collings, trustee), U. S. Patent 1,735,420, Nov. 12, (1929). The material is treated at ordinary temperature with a 30 per cent solution of hydrochloric acid. An apparatus is described.

245.—A New Process for the Determination of Fiber Mixtures.

P. Krais and M. Markert. *Wochbl. Papierfabr. 62*, Sondernummer 23A, 53-5 (1931). A 1 g sample of the material is heated on a boiling water bath for one hour, with mechanical stirring, in 100 ml of solution containing 100 g crystal calcium thiocyanate. The residue is brought onto a filter of 125 mesh copper screen, washed continuously for 15 to 30 minutes, dried, and weighed. Silk and rayon are entirely soluble; cotton and wool nearly insoluble under these conditions. Wood pulps are partially soluble, hence the method is useless for papers.

246.—Chemical Testing of Wool.

K. Augustin. *Z. ges. Textil.-Ind. 36*, 223-5 (1933). A description of various tests.

247.—Analysis of Cotton-Wool Textiles.

R. T. Mease and D. A. Jessup. *B. S. Jour. Research 12*, 85-86 (1934) RP635. The results of a study of several methods for determining cotton and wool mixtures are presented. The inadequacy of some of the methods is shown, and a satisfactory procedure is described. In this method, sizing, finishing material and natural non-fibrous constituents of the textiles are removed by solvent extraction, followed by digestion with a starch-hydrolyzing enzyme and washing. Wool is determined directly by weighing after removal of the cotton by carbonization with aluminum chloride. Cotton is determined directly by weighing after removal of the wool with potassium hydroxide. Results accurate to within 1 per cent of the amount of total dry fiber are readily obtainable.

248.—The Determination of Textile Fibers.

K. Yamada and T. Noguchi. *J. Soc. Chem. Ind., Japan 37*, Suppl. binding 203 (1934). Solvents for silk, cotton, wool, and rayon were investigated. A 50 per cent solution of calcium thiocyanate is most effective for the separation of silk from the other three materials. Ammoniacal copper oxide solution (0.02434 g of copper and 0.4375 g of ammonia in 5 ml) is effective in dissolving rayon, chiefly viscose and cuprammonium, to separate it from wool and cotton. A 2 per cent solution of sodium hydroxide satisfactorily dissolves wool to separate it from cotton. With these solvents about 7 to 10 per cent by weight of cotton and at most 5.31 per cent of the other materials are lost during analysis, as a result of a certain amount of solvent action of each of the solvents upon all the materials.

249.—Analysis of Textiles for Cellulose-Acetate Rayon, Silk, Regenerated-Cellulose Rayon, Cotton and Wool.

R. T. Mease and D. A. Jessup. *Am. Dyestuff Reptr. 24*, 613-18 (1935); *J. Research NBS 15*, 189 (1935) RP821. Cellulose-acetate rayon, silk, regenerated-cellulose rayon, cotton and wool are determined by extraction of the mixed fibers with carbon tetrachloride, desizing with a starch- and protein-hydrolyzing enzyme and with water, removal of acetate rayon with acetone, and silk and regenerated-cellulose rayons with solutions of calcium thiocyanate of specific gravity of 1.2 and 1.36, respectively. Cotton is determined by removal with aluminum chloride and heat to leave the wool, or by dissolving the wool in potassium hydroxide solution to leave the cotton. The accuracy of the method for each fiber is $\pm$ 2 per cent of the weight of the specimen analyzed.

250.—The Determination of Wool in Wool-Cotton Textile Materials.

B. A. Ryberg. *Am. Dyestuff Reptr. 25*, P296-302 (1936). Existing methods of determining wool in wool-cotton materials are reviewed. A proposed method is based on the treatment of a sample in a 1 per cent solution of sulfuric acid, at the boiling point, followed by a treatment in a 70 per cent solution of sulfuric acid at 38° The sample is prepared by extracting for two hours with carbon tetrachloride and washed in warm distilled water. Approximately 2 g of prepared sample is dried to constant weight (105 to 110°) and immersed in 200 ml of boiling 1 per cent sulfuric acid for 7 to 10 minutes. If the sample is cloth or yarn, it is transferred to a Gooch crucible and the excess acid removed by suction; if in the form of loose fiber, it is collected in a crucible with a medium fritted glass bottom and the excess acid removed by suction. The sample is placed in 200 ml of 70 per cent sulfuric acid at 38° and worked 15 minutes. It is collected on a 100-mesh screen or in a crucible with fritted glass bottom and washed with cold water, placed in a beaker and neutralized with a 2 per cent solution of sodium bicarbonate for 5 minutes. It is washed back on the screen or into the crucible, is ovendried and weighed. Results by the method are compared from five laboratories and show agreement. The Kjeldahl method for determining the nitrogen content of wool as a means of estimating the amount of wool in wool-cotton textile mixtures is less reliable for routine work than the sulfuric acid method. Silk, regenerated-cellulose rayon and acetate rayon all dissolve completely, while tussah silks leave a small residue of woody non-fibrous material.

FULLING

251.—The Felting of Wool.

F. A. Hayes. *Textile World 69*, 193-4, 199 (1926). A review of the theory and methods of felting wool.

252.—A Contribution to the Theory of Milling, I. A Method for Measuring the Scaliness of Wool Fibers.

J. B. Speakman and E. Stott. *J. Textile Inst. 22*, 339-48T (1931). The aim of this work is to give quantitative expression to the shrinkage of wool fabrics in a milling machine. The frictional resistance to motion of the wool fiber is smaller in the direction of the root-end than in the direction of the tip, and the difference between these two values is taken as a measure of scaliness and of the effectiveness of the scales in causing shrinkage in milling.

253.—Theory of Milling, II.

J. B. Speakman, E. Stott and H. Chang. *J. Textile Inst. 24*, 273-92T (1933). The surface scale structure of the fiber is the determining factor in milling, but the fiber length, fineness and crimpiness also affect the rate and extent of shrinkage. For a given wool, the rate of milling shrinkage is determined by milling conditions, particularly as regards temperature and the milling agent used, but the mechanism of the process is not understood. To furnish information on the common observation that the rate of shrinkage is least in water and increases with increasing acidity or alkalinity of the milling agent, a study was made of the effect of different pH values on the rate of shrinkage. On the alkaline side, the milling was most rapid at about pH 10. Soap appears to have a specific action in facilitating milling shrinkage independent of the pH of the medium. To determine whether fiber swelling affected milling properties, the swelling of wool fibers in water at different temperatures was studied. This required measurement of the specific volume of wool in benzene and of the apparent specific volume in water at different temperatures. The methods used are described in detail. Swelling is shown to play no direct part in determining the milling properties of a wool under any set of conditions. The explanation of the part played by acids, alkalies and temperatures in modifying the rate of milling

shrinkage is found in their action in modifying the extensibility and elasticity of wool. It is concluded that for milling shrinkage to be possible a fiber must possess a surface scale structure, be easily stretched and deformed, and possess the power of recovery from extension. Suggestions based on this view and the structure of the wool fiber are given for producing unshrinkable wool.

254.—Researches on Fulling.
J. B. Speakman. *Textile World 83,* 1629 (1933). The industrial significance of recent investigations of shrinkage in fulling is pointed out.

255.—Wool Swelling and Wool Felting as a Function of the pH of the Wetting Solution.
I. E. Götte and W. Kling. *Kolloid-Z. 62,* 207-13 (1933). An apparatus for measuring linear swelling in the plane of the fiber cross section is described. At 20° and swelling time of 30 minutes, standard wool shows a maximum swelling at pH 3.0, a minimum at 5.8, and very marked swelling at 11, due to chemical reaction. At 70°, the maximum is displaced to very low pH, the minimum to 4.3, and the reaction to 9.0. *II. The felting of wool.* Ibid. 213-15. By means of Arnold's method (*cf. Textil-Forsch. 11,* 3 [1930]) the felting of wool was found to decrease linearly with increase in pH.

256.—Theory of the Felting Phenomenon.
R. Brauckmeyer. *Deut. Wollen-Gewerbe 66, Erfahr. u. Forsch. 1,* 38-9 (1934); *Deut. Wollen-Gewerbe 67, Erfahr. u. Forsch. 1,* 45-8 2, 49-52 (1935). Wool fiber differs from all other fibers in its chemical composition as a horny material and in its exterior structure with a scale-like surface. The composition of the wool is responsible for its high stretch and elasticity, low heat conductivity, good resistance to acids and the property of simple fast dyeing with dyes of various types, while the exterior structure is responsible for its fulling and felting properties. A number of incorrect theories on the felting of wool are discussed and errors in the Witt theory are pointed out. A new theory is discussed. During the felting process there occurs a decided displacement of the position of the fibers, which move away from the yarn. The migration begins with the roots. Simple experiments are described and photographs are shown for demonstrating the correctness of the theory. The new felting theory is used to explain in detail the behavior of the wool during actual felting operations. Applications dealing with the use of soap in felting operations, artificial wool, chlorinated wool, and rayon are discussed.

257.—The Influence of Fiber Length on the Milling Properties of Merino Wool.
J. B. Speakman and T. Sun. *J. Textile Inst. 27,* 171-6T (1936).

258.—The Fulling Theory.
M. Loescher. *Deut. Wollen-Gewerbe 68,* 476-8 (1936). The migrating theory as applied to the fulling and felting process is critically discussed. Reply. R. Brauckmeyer. *Ibid.* 478-9.

See 184, 263, 285, 307.

FUNGI (See Bacteria, etc.).

Also 157.

HALOGENATION.

259.—The Chlorination of Wool.
Leo Vignon and J. Mollard *Compt. rend. 142,* 1343-1345 (1906). The authors have examined the action of gaseous chlorine, chlorine water, and bleaching powder, in acid solution on wool, and find that while it is dissolved by the prolonged action of the gas, its properties are modified when the action is limited and it loses 10 per cent of its weight, is dyed more readily, giving deeper and more brilliant tints, and becomes unshrinkable. The chlorine is not fixed by the wool, but it appears to destroy the projecting points (hooks) of the scales, and thus diminish its aptitude for felting and shrinking. At the same time the increase in the acid and basic functions caused by the rupture of certain linkings of amino acids would account for the increase in the tinctorial properties.

260.—Chlorination of Wool.
S. R. Trotman. *J. Soc. Chem. Ind. 41,* 219-24T (1922). Properly chlorinated wool shows no loss in either tensile strength or elasticity. Improperly chlorinated wool shows decreases in these properties, different electrical properties, and an increased affinities for dyes, and it is more readily wetted down. Treatment with a 2 per cent solution of formaldehyde before chlorination decreases the solubility and the loss of weight. Methods of chemical and microscopic examination and the determination of loss in weight are described. The addition of mineral acids to bleaching powder solution leads to the liberation of both hypochlorous acid and chlorine, the proportions depending upon the amounts of acid used. Weaker acids such as acetic and boric acids cause the liberation of mostly hypochlorous acid. Experiments show that damage during chlorination is due to destruction of cortical cells and the complete disappearance of epithelial scales by chlorine. Damage may also be produced during finishing and after finishing, owing to incomplete removal of chlorine, with the consequent breaking down of damaged fibers. Since chlorine damages wool more easily than hypochlorous acid, bleaching powder should be used under conditions producing a minimum liberation of chlorine. Different grades of wool require different treatment and the maximum bleaching solution, applicable to a particular grade should be determined and never exceeded. The strength of bleaching powder when used with mineral acid should rarely exceed 0.6 g of available chlorine per liter. With boric acid considerably stronger solutions may be used.

261.—Dyeing of Chlorinated Wool.
J. R. Adams. *J. Phys. Chem. 27,* 8-4 (1923). Tables and curves show in detail that wool, previously treated with bleaching powder and dried aftere washing with hydrochloric acid, adsorbs typical acid dyes in definite relation to the H-ion concentration of the dye bath. Orange II was adsorbed in the amount of 83.3 per cent of that originally present from a bath at pH 2.55, and to the extent of 1.03 per cent at pH 6.43. The eight intermediate values shown are not far from linear. Acid sodium sulfate in a solution at pH 3.05 had a stripping action affecting 47.1 per cent of the dyestuff used; at pH 2.45, it was 32.3 per cent. The effect with lake scarlet R was very similar, the limiting values of ten determinations showing adsorption to be 95 per cent at pH 2.73, and 1.73 per cent at pH 5.76, the stripping effect of sulfuric acid-sodium sulfate was 31.2 per cent at pH 3.27, and 20 per cent at pH 2.55. Each pH value was determined after the dyeing had been completed. The final concentration of dyestuff in the bath was determined by direct titration with titanous chloride (*Ber. 36,* 1552 (1903); *40,* 3819 (1907). The adsorption curves of chlorinated and of ordinary wool lie very close together; dyeings on the former are much brighter than on the latter, probably owing to the increased glossiness of the chlorinated wool, and possible to the presence of acid in the wool.

262.—Commercial Chlorination of Wool.
L. Meunier and H. Latreille. *Chimie et industrie 10,* 636-42 (1923). Commercial chlorination of wool is carried out either to obtain fabrics which will not shrink and felt when washed with hot soap solutions or in the presence of alkalies, or to obtain proper fixation of colors when printing. It is usually carried out with

bleaching powder solution, and the results obtained are somewhat irregular. According to Trotman damage is due to free chlorine rather than to hypochlorous acid, and irregularities are due to varying amounts and proportions of the two liberated according to the amount of hydrochloric acid added to the chlorinating bath. The action of dry chlorine (dissolved in carbontetrachloride) on dry wool reduces the sulfur content (from 3 per cent to 2.08 per cent in one case). The sulfur removed probably corresponds to half that present as organic disulfide (-S-S-), *e.g.,* cystine. According to Knecht and Milnes (*J. Soc. Chem. Ind.* 1892, 131) and H. Pearson (*J. Soc. Dyers Colourists 81,* 1909) dry chlorine has practically no action on dry wool; but Meunier and Latreille found that dry wool fixes up to 5 per cent of dry chlorine (either as gas or in solution in carbontetrachloride) which is then present as chloramine (RCONCIR') and as hydrochloride (RCONH(HC1)R') in equal amounts, and probably also to a slight extent substituted in the benzene nuclei. The total loss in weight of wool after chlorination, washing with benzene, water, sodium bisulfite, and water was less than 0.5 per cent. Treatment with chlorine, gas of wool containing moisture causes damage in proportion to the amount of water, which is not due to the formation of chloramines, but to the oxidation of the protein matter in the presence of water. In commercial chlorination with bleaching powder, the greater proportion of the available chlorine oxidizes the wool and is not fixed by it but remains in the spent liquor. Serge which had been chlorinated dry shrank less on washing than unchlorinated samples and samples chlorinated with their normal moisture content. It is shown that dry chlorination decreases the contact surface tension between wool and water, so that capillary phenomena take place more rapidly. On the other hand, the swelling power of the chlorinated fiber is reduced, which shows that it has undergone a true tanning. The rate of fixation of both basic and acid dyes by wool which has been dry chlorinated, washed with water, sodium bisulfite and water is increased, but the shades are not fast to washing. On a commercial scale the wool could be dried by passing a current of dry air at 85° over it for 20 minutes, and while still hot treated for 12 hours with 5 per cent of its weight of dry chlorine gas. It is then washed with water, 1 per cent sodium bisulfite and finally with water.

263.—Unshrinkable Finish on Wool.

S. R. Trotman. *Am. Dyestuff Reptr. 12,* 611-2 (1923). Theories relating to shrinking and felting are discussed, as well as the properties of chlorinated wool.

264.—The Unshrinkable Finish Process.

S. R. Trotman. *J. Soc. Dyers & Colourists 39,* 359-60 (1923). Stock which has previously been damaged by disease, bacteria, carbonizing, scouring or in any other manner is much more susceptible to injury by chlorine than the normal wool. The chlorine acts upon the fiber by dissolving the amino compounds and converting the combined sulfur into sulfuric acid.

265.—Action of Ozonized Air on Wool and on Chlorinated Wool.

S. R. Trotman and D. A. Langsdale. *Chemistry and Industry 42,* 13T (1923). Samples of woolen yarns and fabrics were exposed to the action of ozonized air side by side under a bell jar with portions of the same materials previously chlorinated. Ozonized air was passed into the jar for 15 minutes during eight consecutive days. Microscopic examination of the fibers showed that the outlines of the epithelial scales became gradually less marked and the scales disappeared and exposed the cortex. Chlorinated wool or wool damaged in scouring was more quickly attacked than ordinary untreated wool. Destruction of epithelial scales to the extent of 25 per cent was accompanied by a loss in felting power. Treatment with ozonized air caused in all cases an increase in the matter soluble in 0.1 *N* sodium carbonate solution. This action was also greater with the chlorinated or damaged fiber. After ozonizing, the samples were washed with water and very dilute alkali and the soluble sulfur was determined. There was a loss of sulfur in every case, the loss being greater with chlorinated or badly scoured wool. Any process such as chlorination or alkali damage which renders the wool more sensitive to chemical action increases the rate at which it is attacked by ozonized air. Wool damaged by ozone has properties similar to those of over-chlorinated wool.

266.—The Amino-Nitrogen Content of Wool in Relation to Chlorination.

S. R. Trotman and C. R. Wyche. *J. Soc. Chem. Ind. 43,* T293-5 (1924). Wool contains both alipathic and aromatic amino groups. The total amino-nitrogen probably is about 0.7 per cent. The total amino-nitrogen is greater than that lost by deamination, hence probably imino groups are present. The Liebermann reaction gives inconclusive results with wool. Ordinary and deaminated wool have the same shrinkage, elasticity and tensile strength, and absorb practically the same amount of chlorine. During the chlorination of wool, chlorine is both adsorbed and enters into chemical combination. The prolonged action of chlorine gives rise to sulfuric acid and soluble nitrogen compounds. The latter contain firmly combined chlorine and are decomposed only by prolonged boiling. The chlorinaated wool contains approximately 6 per cent of chlorine, which cannot be removed by means of hydrogen peroxide, and which is expelled only by boiling.

267.—Chlorination of Wool.

J. B. Speakman and A. C. Goodings. *J. Textile Inst. 17,* T607-14 (1926). The reduction of shrinkage obtained by chlorination of wool is due to the formation of a layer of jelly between the unattacked cortex and the cuticle of wool by the consecutive actions of chlorine and soap or soda. The poor wearing properties of unshrinkable wool are due to the ease with which the jelly layer and its surrounding scales are removable by friction. A process, applicable only to dyed goods, has been devised for shrinking and hardening the jelly layer to the unattacked part of the cortex and thereby improving the wearing properties of the wool. Absolute unshrinkability is attainable under particular conditions. The limiting factor in this respect is the difficulty of insuring even chlorination of all fibers, especially where yarns are concerned, on account of the preferential absorption of chlorine by the outside fibers.

268.—Further Experiments on the Chlorination of Wool.

S. R. Trotman and E. R. Trotman. *J. Soc. Chem. Ind. 45,* T111-5 (1926). The action of chlorine on wool is complex. Only a small portion of the chlorine taken up by the wool enters into chemical combination with the wool under those conditions by which an unshrinkable finish is generally produced. A more thorough understanding of the action of chlorine on wool is necessary to reach a satisfactory control of the "unshrinkable" process.

269.—Visible Changes in Wool Following Chlorination.

A. Herzog. *Melliands' Textilber, 9,* 33-8 (1928). A thoroughly illustrated microscopical study. The chlorinated wool exhibits three radial layers; an epidermis (*I*) which differs slightly from an inner layer of chlorinated cortex (*II*), and an inmost unchlorinated cortex (*III*). The relative thicknesses of *II* and *III* measure the time of immersion in the acidified hypochlorite solution. In aqueous mounting, or in glycerol or balsam, *I* and *II* are readily seen to be much more refractive than *III*. Basic dyes color *I* and *II* much

more deeply than they do *III*. In chloral hydrate, cuprammonium reagent, ammonium hydroxide, concentrated acetic acid, and 10 per cent sodium carbonate *I* is not dissolved but is much crumpled and shrunken, *II* rapidly loses refractive power and dissolves, and *III* splits apart. Differences are also noted with concentrated sulfuric acid, 1 per cent osmic acid, and zinc chloride plus iodine, but not glycerol.

270.—The Action of Chlorine and Hypochlorous Acid on Wool.

S. R. Trotman, E. R. Trotman, and J. Brown. *J. Soc. Chem. Ind. 47,* 4-8T (1928). The present work furnishes additional evidence of the difference in action between chlorine and hypochlorous acid on wool and also gives evidence of a fundamental difference between the actions of hypochloric acid and sulfuric acid on wool. Chloramines are formed when chlorine acts on wool, but cannot be detected when hypochlorous acid is the chlorinating agent. When treated with hypochlorous acid, wool loses its power to condense with semicarbazide, but when treated with chlorine in the presence of hydrochloric or sulfuric acid, it still contains carbonyl groups which can form condensation products with semicarbazide. In the presence of sulfuric acid, wool loses more nitrogen and is able to combine with more semicarbazide than in the presence of hydrochloric acid. This difference is not due to the action of the acids for 0.075 mole per liter of either hydrochloric or sulfuric acid has no effect on the nitrogen content of wool. To study the varying behavior of wool when chlorinated under different conditions, variation in the amino-nitrogen content was studied. The apparatus and method of determination are described. The action of chlorine on wool is to effect a scission of the amino-nitrogen and is not affected by the presence or absence of sulfuric acid. The presence of hydrochloric acid apparently acts as a protection against this action of chlorine, the reaction in this case appearing to be a dissolution of the wool substance as a whole. The action of hypochlorous acid is still less pronounced but it also appears to cause a slight disslution of the wool as a whole. The epithelium is less affected in the presence of sulfuric, which reacts with the cortex to a greater extent than does hydrochloric acid.

271.—Unshrinkable Finish in Woolen Knitted Goods.

S. R. Trotman. *Textile Mercury, 82,* 429, 479 (1930). The chlorination of wool to obtain an unshrinkable finish in hosiery manufacture is described and the theory of the process is discussed. Methods suggested for testing chlorinated goods are: (1) Determination of damaged fibers: Mount well-separated fibers and examine microscopically, making total count. (2) Measurement of shrinkage: Fold a piece into a square 12 by 12 inches and sew the free edge. Measure exactly the length and the breadth, boil one-half hour in 5 per cent aqueous solution of olive oil soap, occasionally pressing together. Wash with hot water, dry and remeasure. Calculate difference in area before and after boiling as percentage shrinkage. (3) Solubility test (for wearing power): Determine percentage solubility in dilute alkali. Soak 2 g fabric for six hours at room temperature in a stoppered glass bottle with 100 ml 0.1 *N* sodium carbonate. Filter off the liquid and weigh the dry residue from an aliquot. Determine dissolved protein by the biuret reaction. Acidify 5 ml of filtrate with hydrochloric acid and boil one minute in a test tube to expel hydrogen sulfide, cool, wash into a graduated cylinder, add a definite volume of standard copper sulfate solution and dilute to 50 ml with dilute sodium hydroxide. Let the precipitate settle and observe the presence and depth of color of the supernatant liquor. The depth of color is proportional to the content of protein.

272.—Chlorination and Deterioration of Wool.

Russina. *Melliand Textilber. 12,* 404-6 (1931); *13,* 207-9 (1932). In chlorinating wool the active chlorine is transformed into hydrochloric acid. The chlorine content decreases to an amount dependent on the volume of the bath but not on its concentration. In determining deterioration of wool the strength of the wet material is much more characteristic than the strength of the dry goods. In treating with alkaline solutions the amount of sulfides or of sulfur, respectively, dissolved from the wool increases continuously, provided the alkali concentration remains low enough, while the biuret reaction is negative even after several days. A method is given for determining decomposed wool by extraction with potassium hydroxide and nitrogen determination according to Kjeldahl or by oxidation with chromium trioxide. In acid treatment the deterioration of wool is increased with increasing acid concentration. However, prolonged boiling is more deleterious than higher acid concentration. In chlorinating even with high chlorine consumption a decrease in the strength in wet condition was not observed.

273.—Further Experiments on the Unshrinkable Finish for Knitted Woolen Goods.

S. R. Trotman. *J. Soc. Chem. Ind. 50,* T463-7 (1931). Experiments were carried out on various methods of reducing the structural damage resulting from the use of chlorine and hypochlorous acid to reduce the shrinkability of knitted woolen goods. Trials of different methods of producing the chlorine (*e. g.,* potassium persulfate plus sodium chloride and Aktivin plus hydrochloric acid) led to the conclusion that it is impossible to render wool unshrinkable by means of chlorine without damaging 20 to 30 per cent of the fibers. With hypochlorous acid, fairly good results were obtained when the hypochlorous acid was produced by adding sodium acid pyrophosphate or Turkey-red oil to bleaching powder or sodium hypochlorite. Less successful results were obtained with rosolic acid, aluminum sulfate, and magnesium chloride as acidifiers. Several protective agents were tried. Pretreatment with benzoquinone increased the resistance of wool to chlorine. Gelatin and glue had a protective action with hypochlorous acid, but not with chlorine. Phenols also reduced damage when hypochlorous acid was used. Attempts to produce unshrinkability without chlorine were not entirely successful, but some positive results were obtained with metallic oxides, gelatin tannate, zinc chloride and borax. The use of zinc chloride combined with light chlorination is suggested.

274.—The Use of Aqueous Solutions of Chlorine and Bromine for the Production of the Unshrinkable Finish on Knitted Woolen Goods.

S. R. Trotman. *J. Soc. Chem. Ind. 52,* 159-64T (1933). Neutralized chlorine water, which is quite free from acid, produces practically no damage, while the addition of small amounts (0.1 per cent) of hydrochloric acid causes a great increase in damage. An excess of hydrochloric acid has no further detrimental action. The presence of sodium chloride exercises a protective action especially when 5 per cent chlorine was used. While the presence of iron and copper (10 ppm.) in chlorine water caused no increase in damage, the same amount of manganese caused marked increase in damage. The damage at 100° F. is no greater than at atmospheric temperature and is recommended because better penetration is obtained and much less chlorine is required. Bromine reduces shrinkage similarly to chlorine and produces much less structural damage than the equivalent quantity of chlorine. A small proportion of bromine added to chlorine water will reduce the damage considerably.

275.—The Processes in the Reaction of Halogens Upon Wool.

H. vom Hove. *Angew. Chem. 47,* 756-62 (1934). In the reaction of dry chlorine, bromine, and iodine, in the gaseous state or in non-aqueous inert solvents, upon completely dry wool only a small amount of chemical reaction takes place with the wool protein (substitution). Halogens with normal moisture content are adsorbed by dry wool with haloamine formation. Furthermore some substitution and a small amount of oxidation of wool protein takes place. In aqueous solution a very rapid consumption of chlorine and bromine by the wool takes place, where the halogens go through the hypo-acid and haloamine stage and effect a hydrolytic splitting of the wool protein by oxidation and haloamine decomposition with formation of the corresponding halo-hydrogen acids. The resulting peptones, polypeptides and reactive amino groups immediately enter into a chloroamine or bromoamine formation. From the halo-amines, hydrochloric and hydrobromic acids are formed, which effect new hydrolytic splitting, etc. At the same time active halogen penetrates to the interior of the fiber, where it forms halogen-hydrogen acid with water, which oxidizes the fiber. A substitution of the halogens in the tyrosine of the wool protein takes place also. The resulting halogen-hydrogen acids give rise to a Donnan membrane equilibrium and the blistering of the fiber surface known as von Allwörd's reaction. With iodine the oxidation at the fiber surface is considerably slower than with the other halogens, so that iodine penetrates almost exclusively by adsorption from the solution to the interior of the fiber, where it slowly forms hydriodic acid. The amounts of halogen substituted in the tyrosine of the wool protein increase with rising initial concentration of the halogen solutions in the ratio of simple multiple proportions, to a maximum value which is six times that of the smallest found halogen content. The increased dyeing capacity of halogenated wool is due to the destruction of the outer fiber layer, thus exposing the interior of the fiber to the dyes. The destruction of wool effected by the oxidizing action of the halogens increases with rising halogen concentration and has been confirmed by tear-strength tests.

276.—The Chemical Treatments of Wool Fiber, III. Treatments Analogous to Hypochlorite Chlorination.

H. Sobue and Y. Hirano. *J. Soc. Chem. Ind. Japan 37,* Suppl. volume 427-30 (1934). The oxidizing power of calcium and sodium hypochlorites is very strong on account of the hypochorite ion. The wool loses weight in the hypochlorite solution, as the oxidized wool dissolves in weak solutions of alkali. The solubility of wool increases with the basicity of the treating liquid. In the chlorination of wool, the strength and elongation decrease in general.

277.—Properties of Chlorinated Wool and the Determination of Damage in Chlorinated Knitted Woolen Goods.

S. R. Trotman, H. S. Bell and H. Saunderson. *J. Soc. Chem. Ind. 53,* 267-73T (1934). The authors have made quantitative experiments with scoured wool and the same wool after chlorination in such a way as to produce varying quantities of damage. Both yarn and web were used. Experiments were made with acid, basic, direct, mordant and vat dyestuffs. The quantitative data point to the fact that the chlorinated samples took up more of these different types of dyestuffs than the unchlorinated. Experiments with fabrics and yarns containing increasing percentages of damage indicated that a determination of the dyestuff absorbed under standardized conditions should give a measure of the damage. Experiments were conducted with kiton Red G and the results clearly indicated the ability of the method to distinguish between good and bad samples. It is to be noted, however, that for percentages of damage exceeding 50 per cent, the absorption of the dyestuff does not increase proportionally. This is not of great importance since any fabric showing 50 per cent of damage must be regarded as deficient in wearing power. The method for carrying out this test is described and it has been found that the limit for absorption of untreated samples is 0.140 to 0.187 millimole per 100 g, with a mean value of 0.162 millimole. The maximum percentage of damaged fibers for a well-chlorinated sample is 25 to 35 per cent, which corresponds to an absorption of 0.25 and 0.35 millimole per 100 g, respectively. When the absorption reaches 0.4 millimole per 100 g, over-chlorination is probable. An absorption exceeding 0.4 millimole is conclusive evidence of at least 50 per cent damage. Similar experiments were conducted with indigo carmine. Quantitative data are also given on the affinity of chlorinated wool for water, and it was found that the affinity increased slightly with moderate chlorination, but decreased with over-chlorination. Neither the solubility in sodium carbonate nor the amount that goes into solution shows any direct relationship to the degree of damage.

278.—Halogenation of Wool.

C. Courtot and A. Baron. *Compt. rend. 200,* 675-6 (1935). The treatment of wool with chlorine or bromine causes marked morphological changes, while iodine is practically inactive although definite adsorption occurs. Long exposure to an excess of chlorine or bromine but not iodine in water causes 60 per cent of the wool to dissolve. Oxidation of sulfur does not affect the solubility. Solution by chlorination or bromination produces a change in the polarization of light. On steam distillation the neutralized solution yields a mixture of aldehydes. Thoroughly washed chlorinated wool has an oxidizing power 30 times that of the chlorine present.

279.—The Use of Aqueous Solutions of Bromine for the Production of the Unshrinkable Finish on Knitted Woolen Goods.

S. R. Trotman and H. S. Bell. *J. Soc. Chem. Ind. 54,* 30-3T (1935). Neither loss of tensile strength nor diminution of extensibility was produced by bromination. The capacity of brominated wool for absorbing water and alkaline solution was not much different from that of the untreated sample. Brominated wool is between untreated and chlorinated wool in regard to the absorption of direct and mordant dyes, but much more like untreated than chlorinated wool. However, the affinity of brominated wool for basic dyes is practically the same as that of chlorinated wool, both absorbing the dye readily from a cold solution.

280.—The Action of Halogens on Wool.

R. Haller and F. W. Holl. *Melliand Textilber. 17,* 493-5 (1936). This is a review of the action of chlorine and bromine on wool. One g of wool combined with about 0.430 g of iodine when soaked in an alcohol-water solution of iodine for 15 hours (saturation). The wool was dark red-brown in color. When it is boiled in water until it becomes bright yellow it no longer gives a starch test for iodine. The yellow color is fast to light, washing, fulling, and alkali. With an excess of iodine, the amount of chemically combined iodine reaches a maximum of 6.5 per cent in 20 minutes. Chemical combination takes place only in aqueous solution or in the presence of traces of moisture.

See 40, 150, 151, 316, 346.

HEAT, Effect of.

281.—Chemical Decomposition of Wool at 100°.

J. L. Raynes. *J. Textile Inst. 18,* T46-7 (1927). The longer the time that samples of wool were dried at 100°, the lower the nitrogen value. Wool extracted with alcohol and washed with warm water was squeezed to remove the excess of water and

sealed in a glass tube. After heating at 100° for 48 hours the tube was broken under dilute acetic acid. There was a pressure of gas in the tube and hydrogen sulfide and ammonia were evolved. Neutral wool was prepared and was heated to 100° in a current of ammonia-free air in an apparatus arranged to retain any ammonia evolved. The nitrogen evolved as ammonia was 0.2176 per cent of the weight of the dry wool. Even cold water causes a slight hydrolysis of the wool fibers.

282.—The Effect of Heat on Wool Fibers.

K. Stirm and P. L. Rouette. *Melliand Textilber. 16,* 4-6 (1935). Raw wool fibers carefully spun to yarn, without having been subjected to heat, chemical or mechanical effects, were heated in a thermostat provided with humidity control. The effects of four factors, temperature, time, humidity and pH value, were determined. The amount of ammonia evolved by the yarn was taken as a measure of the decomposition of the wool. Curves are given which show the amount of ammonia as functions of the four factors. With increasing temperature especially above 100°, the ammonia rapidly increases. The temperature curves are flat at first, then become steep above 100°. The curves showing the amount of ammonia as a function of the duration of the test for various temperatures are steep at first and then flatten out. The ammonia also increases with increasing humidity. Wool yarn treated with alkali evolves more ammonia on heating than wool treated with acid. In a second group of curves the amounts of hydrogen sulfide evolved from wool when heated are given as functions of the four factors. The curves are similar to those obtained for ammonia. Wool subjected to heat shows, under ultraviolet rays, a greenish yellow fluorescence. Curves are also given showing the decrease in tensile strength and the change in thickness of wool yarns subjected to different temperatures for various lengths of time.

283.—The Effect of Heat on Wool.

M. C. Marsh. *J. Textile Inst. 26,* T187-96 (1935). An apparatus for heating wool over a period of time without attention is described. With it, a temperature up to 180° can be maintained with an accuracy of ±½° and the humidity can be controlled. Tests were conducted on 1/30's dry-spun worsted yarn and 60's insulating cotton yarn at 100°, 120°, 140°, 160° and 180°, each with dew points of 30°, 50°, and 70°. Changes in strength, extension at break, weight and color were noted. Increasing temperature causes a decrease in the strength, extension and weight of both wool and cotton. Above 100°, a change in color generally occurs. The humidity during the heating period has little effect on strength and extension. High dew points tend to prevent a loss of water at lower temperatures, but cause a decrease in the subsequent hygroscopic capacity. Prolonged heating causes serious damage only when there is some deterioration in a short time. If the temperature is high enough to cause damage, this will go on progressively during the heating period. At high temperatures, wool is less damaged than cotton, and the rate of deterioration is less.

HEAT OF COMBUSTION.

284.—Heats of Combustion of the Chief Nitrogenous Compounds in Living Organisms, and Their Relation to Animal Heat.

Birthelot and André. *Compt. rend. 110,* 925-34 (1890). I g of wool burns with liberation of 5567 cal.

See 217.

HEAT OF HYDRATION.

See 326, 333.

HEAT OF NEUTRALIZATION.

See 24, 313.

ISOELECTRIC POINT.

285.—Determination of the Isoelectric Point of Wool and of Silk. Applications.

L. Meunier and G. Rey. *Compt. rend. 184,* 285-7 (1927). The point of minimum swelling exists at pH 3.7 for wool, and at approximately 4.2 for silk. The latter point is much less distinct. It is concluded that silk contains fewer amino and carboxyl groups, since it is less amphoteric and its capacity for combination with acids and bases is less marked than that of wool. Determination of the amino nitrogen in the two fibers as well as the difference in their reaction with quinone and the hydrolyzing enzymes verifies this conclusion. The curve is useful in predicting the shrinkage of wool when worked in liquids of different pH values. Experiments prove that the minimum shrinkage and felting occur in liquors of pH corresponding to the isoelectric point.

286.—The Isoelectric Point of Wool.

M. Harris. *B. S. Jour. of Research 8,* 779-786, (1932) RP451. Suspensions of solvent-extracted Idaho and Australian raw wool and of scoured worsted cloth in buffer solutions of different pH were prepared by grinding the dry wool to a fine powder and shaking the powder in the buffer solution. Electrophoretic measurements of these suspensions gave an isoelectric point for each wool at pH 3.4. The samples were slightly different in nitrogen content. If this is indicative of a difference in structure of the wool, the results indicate that the isoelectric point is very slightly or not at all affected by small differences in constitution. The theory and application of electrophoresis measurements to suspensions of wool are discussed.

287.—The Combination of Silk and Wool with Positive and Negative Ions.

M. Harris. *B. S. Jour. Research 10,* 475-8 (1933) RP453. Wool, with an isoelectric point of pH 3.4, combines with negative ferrocyanide ions in solutions ranging in pH up to about 5.0 and with positive nickel ions in solutions ranging in pH down to about 2.0. Evidently amphoteric proteins combine with both positive and negative ions over a certain range on both sides of the isoelectric point. The extent of this "isoelectric region" depends upon the ions employed as well as upon the protein. The limiting values obtained for the pH at which ions combine with a protein do not necessarily represent the isoelectric point of the protein.

288.—Strength of Wool Yarns in the Isoelectric Region.

J. H. Skinkle. *Am. Dyestuff Reptr. 23,* 1-2 (1934). The breaking strength of wool is highest at its isoelectric point of pH 3.2.

289.—The Isoelectric Point of Wool.

A. Wahl. *Rev. gén. mat. color, 39,* 37-8 (1935). The isoelectric point of wool is at pH 5.8.

See 14, 15, 16, 17, 86, 207, 208, 212, 375, 386, 387.

LIGHT, Effect of.

290.—Development of the Amido Group in Wool.

C. M. Whittaker. *J. Soc. Dyers Colourists 30,* 149 (1914). Flannel, exposed without screen for a month or more, then scoured with soap and ammonia was found to have considerably altered dyeing properties. The affinity for basic dyes is considerably increased; and the affinity for acid dyes in most cases is considerably decreased, but the stronger the acid used in the dyeing the more nearly the affinity approaches normal. Exposed flannel when diazotized and coupled with α-naphthylamine had a much lighter shade than results with the unexposed flannel. Whittaker assumes that

the amido groups are destroyed during the exposure, and further states that although his results are confirmed in three successive summers, they are in direct contradiction to the everyday experience of garment dyers.

291.—The Action of Atmospheric Agencies Upon Wool Fabrics.

A. Kertess. Main Kur. *Farber-Ztg. 30,* 137-41 (1919). Exposure to light destroys scoured wool most rapidly, dyed wool next, and wool treated with chromium salts least rapidly. The use of chromium salts for improving the resistance of wool has been patented by Rechberg Co. (Ger. Pat. 286,-340, Dec. 1913. Acid salts, alum, or iron salts have some useful effect but are inferior to chromium salts. Even the latter only retard the action of light and air, as was proved by the failure of much of the uniform-cloth in the summer campaigns of the war. In cloth composed of white wool mixed with a dark dyeing, the cloth becomes progressively darker, because of the destruction by light of the white wool, which is attacked first, and falls away owing to its friable character (in 3 to 4 months). After a few months more, the whole fabric has become tender. Coat and trousers materials exposed for eight months on boards to exclude mechanical effects behaved similarly. Various treatments of undyed wool fabrics were tried, the samples being exposed on boards. The softer the handle of the goods treated, the more marked was the action of weathering. Fats and lanolin proved to be harmful additions. Chrome oxide is the most desirable compound to improve the resistance of wool. Prolonged action of ozone weakens wool, but the fibers remain soft and elastic. The presence of chromium compounds did not decrease the action of ozone. Illumination with ultraviolet light gives accelerated changes similar to those caused by weathering. The biuret reaction is useful for determining the extent of the injury caused by weathering. Wool exposed to atmospheric agencies becomes acid in reaction, owing to the oxidation of soulfur to sulfuric acid. Silk is destroyed similarly, but does not react acid, since no sulfur is present to form sulfuric acid. A test, in addition to the biuret reaction, is furnished by dyeing with methylene blue at 50°. The altered wool is more deeply colored than that which is not changed.

292.—The Effect of Atmospheric Influence on Cloths and Woolens.

A. Kertesz. Main Kur. *Z. angew. Chem. 32,* I, 168-70 (1919). Chromed wool stands up much longer than untreated wool, while dyed wool is intermediate. Numerous experiments are reported to prove these points. The character of the disintegration of wool by ozone was found to be entirely different from that caused by atmospheric influences. Ultraviolet light gave results similar to those obtained in the atmosphere. The albuminoid molecule seems to be disintegrated by air and moisture.

293.—The Injury of Textile Fibers by Light and Weather.

H. Sommer. *Z. ges. Textil-Ind. 30,* 465-8, 482-3 (1919), *Chem. Zentr. 11,* 1417, (1927). The destruction of fibers which occurs on weathering is a process which takes place largely on the surface exposed to light and is due to the short wave lengths. principally ultraviolet rays. Moisture, contrary to previous opinions, furthers the deterioration, especially with wool and bast fibers. The composition of the atmosphere is likewise a factor; the purer the atmosphere the less the destruction. The sensitivity of the investigated fibers to weathering varies greatly. Expressed in the hours of sunshine which are required to cause a loss of 50 per cent in tensile strength they fall into the following order: silk (200), jute (400), artificial silk (900), cotton (940), flax (990), hemp (1100), raw wool (1120), chromed wool (1900). In this evaluation the different thickness of the substances were not taken into consideration.

294.—The Action of Atmospheric Agencies on Wool and Fabrics.

K. Wagner. *Farber-Ztg. 31,* 52-3 (1920). Very soft wool fabrics, such as pilot-cloth or light batiste, which had been exposed to light extensively and redyed in a neutral salt bath, frequently lost their strength and became stiff and brittle. The fibers appeared as though they had been coated with glue or some glass-like sizing. Even in the dye-bath, the fibers had this appearance. From the worst pieces a colloidal mass could be stripped. The same phenomenon was observed by placing a new wool in solutions of sodium hydroxide. Direct dyes which contained some sodium hydroxide added by the maker gave the effects even more markedly. A bath which was slightly acid with acetic acid gave better results. Good results could be obtained only by using those acid dyes which give level dyeings with 2 to 3 per cent of sulfuric acid (on the weight of the fabric), or the corresponding quantities of acetic or formic acid. The portions of the fabrics which had been exposed most were most deeply colored. Bleaching with hydrogen peroxide or "Decroline" occasionally produced level shades. Union fabrics are dyed with acid dyes for the wool, topped in a lukewarm bath for the cotton or boiled out in an acid bath, rinsed, and dyed in a neutral bath with union dyes. When put into a neutral or alkaline bath, the colloidal character of the wool in the portions that have been strongly exposed to light suggests that a disintegration of the protein molecule has been effected, and this is carried further by the alkali. Acids act as coagulating agents and prevent the solution of the altered wool substance. These facts are in harmony with the experiments of Kertess.

295.—Wool Fiber Tips and Their Action in Dyeing.

W. Von Bergen. *Textilber. 4,* 23-5, 17-80, 123-6, (1923). In dyeing certain wools in the hyposulfite-indigo vat, it was noted that the points or tips of the wool fibers were dyed much less deeply than the main portions of the fiber. Similar wool dyed with anthracene chrome brown SWN (Cassella) also dyed unevenly, but the tips were darker than the remainder of the wool. By scouring and dyeing on a small scale samples from various portions of a whole fleece it was found that only the wool from the back showed the uneven effect. This indicated that sunlight caused a chemical change in wool. By exposing a wool which dyed evenly to sunlight, it was found possible to duplicate the effect. Very small differences in the constitution of colors alter their behavior with respect to these wool tips. Eriochromeazurol B leaves the tips lighter, while eriochromecyanin R dyes them deeper than the other portions.

296.—The Influence of Light on Textile Fibers.

P. Waentig. *Z. angew. Chem. 36,* 357-8 (1923). Wool poor in fat was more sensitive to light than silk and cellulose fibers. Tests with exposure of wool to sunlight were made but little change in the properties of the fibers was noticed. Even the assumption that lamb's wool is especially sensitive to light was not confirmed. Cotton, linen, and mercerized cotton are sensitive to light. Viscose silk, nitro silk, and "copper silk" are not nearly so strongly affected, whereas acetate silk shows considerable sensitiveness. Buenos Aires wool showed 12.0 g tensile and 45 per cent elasticity before illumination, 11.7 g and 42 per cent after illumination with a mercury-quartz lamp, and 11.0 g and 45 per cent after exposure to sunlight.

297.—Action of Light on Textiles.

G. Barr. *Trans. Faraday Soc.* 1924, adv. proof. Wool is less affected by light than is silk or cotton.

298.—Damage of Wool Due to Atmospheric Agencies.

P. Heermann. *Chem.-Ztg. 48,* 337-8

(1924). Woolen cloth exposed to wind and weather becomes threadbare in 8 to 12 months. Pure woolen cloth dyed with eight typical dyestuffs were illuminated by: (1) quartz-mercury vapor light; (2) daylight without a glass cover so that only sunlight of longer wave lengths could act on the material. All brought about damage to the wool but in different degrees. The action was a photochemical one caused by light of 2000 to 3500 Å, and the effects of the dyes were probably due to the way they acted as acceptors for impinging rays.

299.—The Action of Atmospheric Conditions on Wool and Woolen Fabrics.
A. Kertess. *Chem.-Ztg. 50,* 661 (1926). Wool exposed to atmospheric conditions, especially sunlight, undergoes a chemical degradation which injures the quality of the cloth. Samples of dye and undyed woolen cloths were exposed to atmospheric conditions for one year. The fibers become brittle, the fleecy oversurface of the cloth disappeared, and the cloth became hard. The initial cloths give very slight biuret reactions (conducted according to M. Becke), whereas the exposed samples give strong biuret reactions, the degree of reaction increasing with the duration of exposure. Dyed samples were more resistant than undyed samples to atmospheric deterioration.

300.—The Action of Ultraviolet Radiation on Wool.
L. Meunier and G. Rey. *Compt. rend. 183,* 596-8 (1926). The acidity and reduction potential of wool are increased by exposure to ultraviolet light. The effects are explained by oxidation of combined sulfur to sulfur dioxide.

301.—Dyeing Properties of Wool Which Has Been Exposed to Light.
W. Von Bergen. *Textilber. 7,* 451-7 (1926). Of 34 dyes which were in a series of parallel dyeings to show the effect of exposure to daylight on the dyeing properties of wool, some showed greater affinity for the exposed wool, some for the unexposed, and with several there was no great difference.

302.—Dyeing Properties of Wool Exposed to Sunlight.
M. Meredith. *Textile Colorist 49,* 739 (1927). Wool which has been exposed to sunlight for some time exhibits considerable difference in dyestuff affinity from the normal wool fiber. In some cases a darker shade is obtained, while in others the shade is lighter.

303.—Effect of Exposure of Wool Before Dyeing.
W. Von Bergen. *The Melliand 1,* 1084-93 (1929). Wool containing acid is more rapidly affected by sunlight than wool which is slightly alkaline. The exposed wool may be either more or less susceptible to dyeing than if unexposed, depending upon the particular color used. Many experimental observations are tabulated.

304.—Method of Determining the Effect of Light on Wool.
W. Von Bergen. *The Melliand 2,* 9-15, 186-92 (1930). As followed on the microscope stage, 0.1 *N* sodium hydroxide causes light-damaged wool to swell and curl more than uninjured fiber. In fact, swelling above 10 per cent may be taken as proof of light damage, and swelling of 100 per cent corresponds to complete destruction of valuable properties.

305.—Yellowing of Wool Under the Action of Ultraviolet Light.
A. Castiglioni. *Chimica e industria 17,* 82-4 (1935). Yellowing is due to the formation of sulfuric acid by the oxidation of the sulfur in the wool. Wool placed in a pan of water and exposed to ultraviolet light is discolored just as with dilute sulfuric acid. Degreased wool tends to turn gray rather than yellow to brown, as untreated wool does. That it, the sulfuric acid formed acts on the cholesterols of the wool. This is confirmed by the fact that a similar color is obtained when cholesterol in chloroform solution is shaken with sulfuric acid. Here a dye is actually formed, as it will dye wool a permanent yellow color.

306.—Oxidation of Wool: Photochemical Oxidation.
A. L. Smith and M. Harris. *Am. Dyestuff Reptr. 25,* 383-4 (1936). *Research NBS. 17,* 97-100 (1936) RP904. The photochemical decomposition of wool has been investigated. The deterioration, as evidenced by the decrease in cystine content and the increase in alkali-solubility, ammonia nitrogen, and sulfate sulfur, is accelerated by acids and decelerated by alkalies. The extent to which wool is degraded during irradiation is directly proportional to the decrease in cystine content and to the increase in alkali-solubility. The sulfur content of untreated and of acid-treated wool decreased during irradiation. The data suggest that a portion of the sulfur in wool is converted to hydrogen sulfide, some of which is subsequently oxidized to sulfuric acid.

307.—The Action of Light on Wool.
P. W. Cunliffe. *J. Textile Inst. 27,* T25-36 (1936). Wool deteriorates during exposure to light as evidenced by decrease in strength and by the Pauly test. Exposed wool becomes more acid, wets out more rapidly, deteriorates more during wet processing, and fulls at a less rapid rate than unexposed cloth.

See 48, 112, 114, 132, 196, 320, 378, 386.

MILLING (See Fulling).

MISCELLANEOUS REAGENTS, Effects of.

308.—The Action of Sulfur Dioxide on Wool.
A. Reychler. *Bull. soc. belg. chim. 23,* 471-5 (1909). Description of an apparatus for measuring the sulfur dioxide absorbed by wool by measuring the pressure under constant volume.

309.—Adsorption of Sulfur Dioxide by Rubber and by Wool.
A. Reychler. *J. chim. phys. 8,* 3-9 (1911). Experiments with wool indicate that 0.88 molecule of sulfur dioxide is combined chemically.

310.—The Action of Quinones on Wool and Other Proteins.
V. Scharvin. Moscow. *Z. angew. Chem. 26,* Aufsatz. 254 (1913). The color is fast to washing and acids and is not affected by boiling ethyl alcohol or by hot glacial acetic acid. Other solvents may be used, or the quinone may be employed as liquid or vapor. Many other quinones dye wool similarly, the velocity of the reaction depending on the particular quinone, the temperature, and the solvent used. Scharvin considers the reaction a proof of the presence of active amino groups in the fiber. The product formed is a substituted aminoquinone, each hydrogen molecule substituted reducing a molecule of quinone to hydroquinone. Analogous compounds have been extensively studied by Zincke and his co-workers. Silk, horn, leather, casein, egg albumin, gelatin, etc. behave similarly.

311.—Influence of Formaldehyde on Wool and the Constitution of Wool.
A. Kahn. *Farber-Ztg. 25,* 73-5 (1914). A 4 per cent solution of commercial formaldehyde protects wool against the action of hot water and alkalies, but destroys almost entirely its affinity for dyes. Much smaller quantities (0.10 to 0.25 per cent) protect the wool in large measure without materially affecting its dyeing properties. The effect is greatest in alkaline solutions. In some instances, mere traces exert a considerable effect. Kahn considers the action to be a condensation of formaldehyde

with wool, and not a catalytic action. Wool treated with nitrous acid condenses with formaldehyde as is shown by the protective action against alkalies, and wool condensed with formaldehyde is yellowed by nitrous acid. From these data, Kahn concludes that wool contains imino and carboxyl groups rather than amino and carboxyl groups, and that the action of nitrous acid yields a nitroso compound, while the hydroxyl group in the carboxyl and formaldehyde undergo an aldol condensation. These conclusions are substantiated by the changes in behavior toward basic and acid dyes which are produced by treating wool in different ways with nitrous acid and formaldehyde. Acetaldehyde acts similarly but less effectively, while acrolein is more efficient than formaldehyde.

312.—Relation Between the Complex Internal Metallic Salts and the Solubility of Silk in Nickelo-Ammoniacal Liquor. Biuret Reaction (Cu, Ni, Co) of Silk and Wool.

M. Battegay and T. Voltz. *Bull. soc. chem. 27,* 536-40 (1920). The reactions of these complex salts with wool are greatly modified when compared with those with silk, the difference being due to the presence of sulfur in the wool.

313.—The Rise in Temperature During the Absorption of Ammonia and Chloroform by Wool.

L. Bleyer. *Arch. Hyg. 94,* 347-52 (1924). The total heat produced during the absorption of ammonia and chloroform by wool, determined experimentally, cannot be explained through heat of condensation alone. The heat of condensation expressed as percentage of total heat, amounts to 40 per cent for ammonia and 50 per cent for chloroform.

314.—Color Reactions of Wool.

L. Meunier and G. Rey. *Cuir 13,* 44-5 (1924). Wool undergoes color reactions when treated with (1) quinone, (2) sodium nitrite, or (3) mercurammine salts. The colors produced under various conditions are described.

315.—Bleaching of Wool with Sulfur Dioxide and Sulfurous Acid. Note on the Presence of a Carbonyl Group in Wool.

J. L. Raynes. *J. Textile Inst. 17,* T379-85 (1926). At least two distinct components of wool combine with sulfur dioxide. One of these, itself apparently colorless, gives a lemon-yellow product, which may be prepared from nearly dry wool and is produced only when a high concentration of sulfur dioxide is used. This substance is unstable and does not appear to be connected with the bleaching effect. The other component of wool combines with sulfur dioxide only in the presence of water and is possibly a colored carbonyl compound which gives a colorless additive product containing the group $C(OH).SO_3H$. This substance is relatively stable in a vacuum but is very slowly decomposed on exposure to light and air, the wool being then discolored. It is slowly decomposed by prolonged washing with water and very quickly by alkalies. The bleaching of wool with sulfur dioxide in the presence of moisture does not depend to any appreciable extent on the reduction of any component by the addition of hydrogen and simultaneous formation of sulfuric acid. The presence of carbonyl compounds in wool seems to be established by the behavior of the material towards hydroxylamine and semicarbazide, but from the fact that wool bleached with hydrogen peroxide still reacts with hydroxylamine, it would seem that both colored and colorless carbonyl compounds are present in the fiber.

316.—Adsorbing Power of Wool for Hydrogen Sulfide and Halogens.

G. Spagnol. *Biochim. terap. sper. 13,* 24-6 (1926). Wool which has been in contact with hydrogen sulfide gas from 15 minutes to three hours and then exposed to air 15 to 30 minutes gave a dark yellow color with lead solution. The hydrogen sulfide was still detectable after 2160 hours. Five to 15 minutes' exposure to a current of chlorine sufficed to impart to the wool an intense iodine-starch coloration after 20 to 30 days' airing, and a delicate tint after 3600 hours. Bromine is detectable after 2600, iodine after 6400 hours' exposure to air.

317.—Adsorption of Vapors by Animal and Vegetable Fibers.

E. V. Alekseevskii. *Zhur. Priklad. Khim. 1,* 184-9 (1928). Nitrotrichloromethane is best adsorbed by dyed new wool and dyed used silk while linen is the poorest adsorbent. It does not affect the fiber strength. Arsenous chloride is best adsorbed by wool, hairs and rubber. Dimethyl sulfate is slowly adsorbed by wool and quickly by cotton and silk, which retain it tenaciously, while wool loses it quickly through evaporation. Benzyl chloride is adsorbed more quickly by animal than by vegetable fibers. Bromoacetone is better adsorbed by animal than by vegetable fibers.

318.—The Action of Formaldehyde on Wool.

S. R. Trotman, E. R. Trotman and J. Brown. *J. Soc. Dyers Colourists 44,* 49-52 (1928). The fabric was immersed in a 0.6 per cent solution of formaldehyde in bottles with wired stoppers. The bottles were covered by a bath kept at 75°. Complete absorption occurred in three hours. The fabric was washed and dried for several days, when the amount of combined formaldehyde was 0.7 per cent on the dry weight of the wool. When heated to 100° the fabric retained all of the formaldehyde. This reaction occurs in 20 minutes or less in an autoclave at 100° or 121°. The combination between wool and formaldehyde is much more stable than that with leather. The protective action of formaldehyde in scouring and various wet processes is slight. Paraformaldehyde has practically the same action on wool as formaldehyde. The nitrogen content of wool is not affected by treatment with acetaldehyde. Formaldehyde wool has an increased resistance to the action of dilute sodium hydroxide or sulfuric acid, to shrinkage, and to the action of bacteria. It has a reduced affinity for neutral and acid dyestuffs. Perhaps the properties of formaldehyde wool are due to the displacement of the peptide equilibrium in favor of the enol form, the latter being more resistant to decomposition by acids and alkalies than the corresponding keto form.

319.—Reaction Between Animal Fibers and Ammonium Chloride Solutions.

A. E. Porai-Koshitz, E. G. Levine, and V. S. Remennikova. *Izvest. Tekstil. Prom. Torgov. 10,* 81-2 (1931); *Chimie & industrie 27,* 909-10 (1932). Meyer recently showed that wool and silk can absorb the anions of acid dyes and of various mineral and organic acids only up to a "limit of absorption," which is 0.008 g for silk and 0.002 g for cotton per g of fiber. Porai-Koshitz found that animal fibers treated at the boiling point with solutions of neutral salts (not acid salts, as in Meyer's investigation) of acid and substantive dyes do not absorb the anions of these dyes; but if the cation (*e.g.*, NH_4) is removed from the field of the reaction, dyeing can be carried out to the limit of absorption as established by Meyer. It was natural to expect that animal fibers would behave similarly not only toward dyes, but toward all salts, the cations of which can be removed from the field of the reactions, such as ammonium salts; and Porai-Koshitz, Gorelkine, and Peskine have shown that wool absorbs hydrochloric acid from ammonium chloride solutions with liberation of ammonia. The purpose of the present investigation was to determine the absorption limit of ammonium chloride solutions by animal fibers. The carefully defatted wool and silk samples were treated in a distilling apparatus with ammonium chloride solutions of different concentrations;

the ammonia liberated was absorbed in 0.1 *N* hydrochloric acid, and the excess of the latter titrated with 0.1 *N* sodium hydroxide. The experimental results showed that the amount of ammonia, corresponding to the amount of ammonium chloride fixed by the fiber, becomes constant above a given concentration of the latter (600 per cent of the weight of the wool and 300 per cent of the weight of the cotton); hence, above these concentrations, the fibers are saturated after prolonged boiling. The saturation limit of 0.008 g per g of wool found by Meyer was confirmed.

320.—The Structure and Some Properties of Wool.

Meunier. *Boll. assoc. ital. chim. tessili color. 7,* 37-9 (1931). Allwörden's reaction is not an absolute proof of the presence or absence of elasticity. The elasticity can be demonstrated by a regulation diastase treatment. By submerging wool in a chlorine solution in carbon tetachloride, a part of the sulfur passes into the solvent as sulfur chloride. Pauly's reaction with benzopurpurin distinguishes well the two proteins in wool. Swelling of wool is minimum in a bath at pH 4.5, maximum at pH 1.5. By tracing a curve of turgescence, characteristic points can be observed. With ultraviolet rays a part of the sulfur in wool is transformed into sulfuric acid. Quinone produces a brown or violet-red color in normal wool and a yellow in wool after exposure to ultraviolet rays. Sunlight produces the same effect in a smaller degree. Dry chlorination if prolonged and followed by rinsing confers the same qualities as wet chlorination. The wool shows no indication of alteration, even when the dry chlorine reacts for longer than necessary. Undried chlorine has an oxidizing action on the fiber, the intensity of which is directly proportional to the moisture content.

321.—Denaturation of Wool by Urea.

W. Ramsden. *Nature 127,* 403-4 (1931). The reaction is due to a union of urea and a derivative of sodium nitroprusside. The reaction occurs in solutions not too strongly alkaline and in the absence of ammonia. Strong urea solutions reveal sulfides in wool when they are alkaline above a certain degree.

322.—Action of Sodium Sulfide on Wool.

J. B. Speakman. *J. Soc. Chem. Ind. 50,* T1-7 (1931). Microscopically, it was shown that the wool cuticle is far more resistant to sodium sulfide than the cortex, and that the reagent produces dimensional changes. Chemically, it was proved that the reaction between wool and sodium sulfide is partially reversible and undergoes rapid acceleration by increases in the concentration of the solution, and time. Neither the elastic phase nor the hygroscopic properties of wool partially destroyed by sodium sulfide were influenced by the reaction, though the permanent set produced by steaming was eliminated. The nature of this set suggests that the disulfide group in wool is masked by an anhydride group, and the action of wool, treated with sodium sulfide, toward water forces the conclusion that the micelles of the wool fiber are lamellae which are attacked and eaten away at the edges, leaving the ratio of surface to mass unaltered. It is also suggested that the disulfide linkage in wool is the point of attack by sodium sulfide, and lies in a plane that makes an angle with the main face of the micelle.

323.—The Effects of Neutral Salts on the Hydrolysis of Wool with Acids and Bases.

E. Kimmel. *Bull. soc. chim. Romania 15,* 121-7 (1933). Pure wool was treated with various concentrations of hydrochloric acid, sulfuric acid, and sodium hydroxide, respectively, in the presence of various salts. By using 0.1 per cent hydrochloric acid and adding sodium chloride up to 100 g, the hydrolysis was only slightly increased; 0.1 per cent sulfuric acid hydrolysis produced a retardation when sodium sulfate is added. Various known concentrations of sodium hydroxide containing sodium carbonate or sodium sulfate caused retardation. When very dilute sodium hydroxide (0.00125 *N*) was used at 100°, sodium carbonate and sodium sulfate have a marked accelerating effect. These salts act as alkalies themselves.

See 245, 260.

MOISTURE, Absorption (See Swelling).

324.—Relation Between the Absorption of Moisture and of Dyestuffs by Textile Fibers.

S. H. Higgins. *J. Soc. Chem. Ind. 28,* 188-9 (1909). Higgins made certain observations which pointed to a connection between the amount of dyestuffs textile fibers are capable of absorbing from solutions and the amount of moisture which those fibers attract from the air. Results of several experiments are recorded in evidence of such a relation.

325.—Absorption of Moisture from the Atmosphere by Wools.

A. M. Wright. *J. Soc. Chem. Ind. 28,* 1020 (1909). The results of the investigation show that the amount of moisture which a wool can absorb from the atmosphere depends upon several factors: (1) The relative humidity of the atmosphere, more moisture being absorbed during a period of high relative humidity than when the humidity is low. (2) Pure wool fiber, of which greasy wool contains 50 to 70 per cent and slipe wool about 75 per cent, can absorb 18 to 20 per cent of its weight of moisture from the atmosphere, but this amount is not sufficient to account for all of the moisture absorbed by the dry normal wool fiber.

326.—Heat of Hydration of Some Textile Fibers.

G. Testoni. *Industria tessile e tintoria 16,* 23 (1915). The fibers, oven-dried and cooled in desiccators, showed a rise in temperature due to absorption of water when exposed to moist air. This rise is almost constant for each kind of fiber, but varies from fiber to fiber. The phenomena were studied by immersing a given weight of dried fiber in a given volume of distilled water, and calculating the increase of temperature on 100 g of dried substance. In the case of fibers like cotton and wool that give sufficiently great differences in temperature rise, this property may be used to determine with good approximation the proportion of the said fibers in mixed threads.

327.—Some Moisture Relations of Colloids, II. Further Observations on the Evaporation of Water from Clay and Wool.

E. A. Fisher. *Proc. Roy. Soc. (London) 103A,* 664-75 (1923). The evaporation of water from woolen fabrics is discussed.

328.—Moisture Relations of Colloids, I. Comparative Study of the Rates of Evaporation of Water from Wool, Sand and Clay.

E. A. Fisher. *Proc. Roy. Soc. (London) 103A,* 139-61 (1923). The absorption of water by wool is attributed to a filling up of fine pores of various shapes and sizes. The vapor pressures of wool-water systems are determined by the diameter of the pores that are full of water.

329.—Thermodynamics of Water Absorption by Textile Materials.

S. A. Shorter. *J. Textile Inst. 15,* T328-36 (1924). Theoretical discussion.

330.—Hygroscopic Capacity of Wool in Different Forms and Its Dependence on Atmospheric Humidity and Other Factors.

S. A. Shorter and W. J. Hall. *J. Textile Inst. 15,* T305-27 (1924). Different forms of the same material showed in certain cases small but unmistakable differences. Yarns and tops gave the same results.

Noils were found to be less hygroscopic because of the presence of foreign matter. Oil was found to diminish the regain of wool. The oil apparently exerts practically no effect on the moisture-absorbing power of the wool, produces a diminution of the calculated regain merely by loading the material with a non-hygroscopic substance. Cloth pieces were found to show wide variations of regain. This result is to be expected owing to the drastic nature of certain finishing processes.

331.—A Review of Work on the Absorption-Desorption of Moisture by Textile Materials.

A. R. Urquhart and A. M. Williams. *Trans. Faraday Soc. 309,* 1924. A review.

332.—The Absorption of Water by Colloidal Fibers.

J. J. Hedges. *Trans. Faraday Soc. 22,* 179-93 (1926). Theories of the mechanism of absorption are given.

333.—Moisture Relation of Colloidal Fibers.

J. J. Hedges. *J. Textile Inst. (Special issue) 18,* T350-9 (1927). Curves for the variation of moisture content of chemically pure wool with atmospheric relative humidity are of the usual sigmoid character given by other hygroscopic colloids. The heat of wetting of dry wool is 24.1 calories per gram. Wool and its absorbed water may be considered as a two-phase system in which a little water is adsorbed by the colloid particles, while the bulk is held in a system of pores. The difference between the apparent (in water) and true sspecific volumes of wool is much greater than that between the corresponding values for cotton, which, in conjunction with the relative values of the saturation moisture contents, points to a much greater contraction in total volume for wool.

334.—Adsorption of Water by Wool.

J. B. Speakman. *Nature 124,* 411-2 (1929). Speakman has shown in previous papers that when wool fibers are held stretched in water the fibrillae within the cells undergo plastic flow and take a permanent set. The present experiments seem to provide an answer to some of the questions raised by King (*Trans. Faraday Soc. 25,* 451 [1929]). The adsorption of water by wool fibers stretched 30 per cent of their length under water (to acquire maximum plastic flow without rupture of the fibrillae) is compared with the adsorption of water by untreated wool fiber. Each sample was taken from absolute dryness up to saturation, in stages, and then in the reverse order to dryness. The stretched samples adsorbed more water in every case than the untreated ones. It thus appears that plastic flow in the fibrillar structure alone will increase the affinity of wool for water.

335.—Effects of Water Treatments and Steam Treatments on the Hygroscopic Properties of Wool Fibers.

N. A. Arkhangelskii. *Niti (Suppl. to Izvestiya Tekstilnoi Prom Torgovli) 1,* No. 3, 11-8 (1930); *Chimie & industrie 24,* 947. Wool treated with water and with steam and untreated wool were conditioned two weeks in an atmosphere at 60 per cent relative humidity and then dried to constant weight at 102° to 109°. While the results obtained so far are insufficient to draw definite conclusions, they indicate that, after conditioning, the water-treated wool contained a little more moisture and the steam-treated wool a little less moisture than the untreated wool.

336.—Adsorption of Water by Wool.

J. B. Speakman. *J. Soc. Chem. Ind. 49,* T209-13 (1930). The adsorptive and desorptive properties of purified wool fibers were studied over a wide range of atmospheric humidities. Marked hysteresis existed between the two processes. The hygroscopic properties of wool were slightly reduced by diazotizing or treating wool with formaldehyde, which proved that free amino acid groups exert an insignificant influence in water adsorption. A comparison of the changes produced in the elastic properties and size characteristics of wool by water adsorption suggests that the fiber is composed of long-chain protein molecules arranged about the long axis of the fiber. Water adsorption is dependent upon the polypeptide groups in these molecules.

337.—The Effect of Temperature on the Moisture Regain of Wool.

A. C. Goodings. *Am. Dyestuff Reptr. 24,* 109-12 (1935). Temperature as well as relative humidities influence the moisture regain of wool. The magnitude of this temperature effect for temperatures within the atmospheric range has been measured at relative humidities ranging from dryness to saturation. Curves and tables are shown and the results summarized as follows: (1) Regain curves have been determined for Botany wool at 10° and 30°; (2) in this temperature range, the regain of wool decreases with increase in temperature, the relative humidity remaining constant; (3) the magnitude of the moisture absorption hysteresis is less at the higher temperature; (4) between the temperature limits investigated, the average change increases with increase in relative humidity up to about 80 per cent relative humidity, followed by a decrease; and (5) the moisture-absorbing capacity of wool increases very rapidly at humidities approaching saturation.

338.—The Adsorption of Water by Wool, I. Adsorption Hysteresis.

J. B. Speakman and C. A. Cooper. *J. Textile Inst. 27,* T183-5 (1936). Adsorption and desorption data on wool at 25° from relative humidities of 10.6 to 89.6 per cent are given. The range of humidity over which wool must be dried to pass from adsorption to limiting desorption conditions appears to be independent of regain and is about 18 per cent. Optimum spinning conditions therefore are obtained by storing tops in a room with a relative humidity of at least 18 per cent higher than that of the spinning room. II. *The influence of drying conditions on the affinity of wool for water.* J. B. Speakman and E. Stott. *Ibid.* T186-90. The adsorption power of wool, dried from regains below saturation, decreases with increasing temperature of drying. The decrease in water absorption is produced by partial as well as complete drying but not by drying from saturation nor heating wool which was dried at low temperature. The normal affinity for water of wool which has been dried at a high temperature is restored by allowing it to reach saturation with water vapor. The reduced adsorptive power of wool heated over water at a high temperature is irreversible. III. *The influence of temperature on the affinity of wool for water.*

J. B. Speakman and C. A. Cooper. Ibid. T191-6. Adsorption isotherms of wool at intervals of 5° from 25° to 55° are given. Complete isotherms above 55° cannot be obtained owing to the susceptibility of the disulfide bond of wool to water at high temperature, as evidenced by formation of mercuric sulfide on the fibers. At low partial pressures of water vapor, the amount of water adsorbed decreases as a linear function of temperature. At partial pressure 0.975 the isobar shows a minimum at about 43°, which indicates that the swelling of wool in water is a minimum near that temperature.

See 366, 378.

DETERMINATION (See Moisture, Adsorption).

339.—The Question of an Accurate Determination of Water in Silk, Wool, Cotton, Etc.

S. Schmansky. *Chem.-Ztg. 36,* 670, (1912). Large apparatus are commonly used for this determination in which 250 to 500 g of the substance is weighed and dried. Shaposhnikov of Kiev has worked out a procedure for smaller amounts, but his apparatus is very complex. He weighs and dries the substance in a U-tube and collects the water in a calcium chloride tube. Results are accurate and reliable.

340.—The Exact Drying of Textile Fibers for Scientific and Technical Purposes.

J. Obermiller and M. Goertz. *Z. angew. Chem. 37,* 940-5 (1924). In determining moisture at temperatures of 105 to 110° for cotton or wool, and of 140° for silk and artificial silk, in ordinary moist air, unsatisfactory results are obtained. Fibers have a hygroscopic power comparable to that of phosphorus pentoxide and so cannot be dried even at 110° in moist air. A certain equilibrium with air is established, which depends upon the temperature and humidity of the air. By means of the apparatus described of *C. A. 17,* 3432, exhaustive tests were made upon all kinds of fibers. When treated in a stream of air dried over phosphorus pentoxide, complete drying of the sample can be attained at even low temperatures; the only influence of the temperature is upon the speed of the process. Other series of tests in air brought to (a) 75 per cent humidity by passing it over moist sodium chloride, (b) 55 per cent by moist calcium nitrate, (c) 35 per cent by moist crystallized calcium chloride, and (d) 2.5 per cent by dehydrated calcium chloride, showed that even at temperatures of 105 to 110° satisfactory drying was not attained. Heating for 3 to 5 hours at 85 to 90° in a current of dried air gave a complete drying for all fibers, without damage to them or to the rubber tubing used for connections, with an accuracy of 0.01 per cent on a 10 g sample. This occurs, too, in spite of minute changes due to side reactions, such as weathering (oxidation), fat alterations, etc.

341.—The Estimation of Water in Wool by Distillation.

C. O. M. Steward. *J. Textile Inst. 24,* T98-102 (1933). A modification of the Dean and Stark distillation method for estimating the amount of water in petroleum is recommended. Perchloroethylene is used in place of xylene or a mixture of xylene and benzene.

MOISTURE, Effect.

342.—Some Effects of Moist and Dry Heat on Wool.

A. Woodmansey. *J. Soc. Dyers Colourists 34,* 227-30 (1918). Hygroscopic moisture may be considered as completely removed if the material is maintained at 100° for 40 minutes, provided there is sufficient ventilation. At higher temperatures the elimination of moisture is more rapid, and when the temperature is raised considerably above the boiling point of water, *e. g.,* 150°, a gradual reduction in the weight of the wool is noticed, owing to the evolution of matter other than water. Prolonged boiling of wool with water produced partial solution of wool substance, with liberation of hydrogen sulfide and ammonia. Dry heat is not nearly so destructive of wool as wet heat. Wool under pressure with water at 130° is completely disintegrated, but dry wool at 200° is weakened less than 7 per cent. When the temperature is gradually raised the first sign of darkening is visible at 145° and the color continues to deepen to 235°, when the material begins to char and fuse. On heating in a current of air, ammonia is evolved and this is increased if in moist condition. Heated wool becomes acid, partly on account of the oxidation of sulfur to sulfuric acid and partly on account of loss of ammonia. The amount of ammonia liberated from wool by heating much above 100° rapidly increases but later on diminishes.

343.—Action of Water on Wool.

A. Reychler. *Bull. soc. chim. Belg. 29,* 291-300 (1920). On heating wool to temperatures up to 150° with water or alkaline or acid solutions under normal or increased pressure, acid or basic substances pass into solution. These are precipitated by fuchsin and form lakes with eosin or ponceau. The undissolved wool loses the property of double refraction between crossed nicols, and can be powdered when dry. If wool is heated to 110 to 120° with water, its elasticity is diminished, but it is still very tenacious, and its plastic properties at these temperatures are utilized in finishing processes. The relative insensitiveness to acids of methyl orange dyed on wool or silk is due to the combination of the indicator with a system which, although not markedly basic, is capable of combining with acid molecules.

344.—The Moisture Content of Wool—Its Relation to Scientific Theory and Commercial Practice.

S. A. Shorter. *J. Soc. Dyers Colourists 39,* 270-6; *Am. Dyestuff Reptr. 12,* 797-803 (1923).) A criticism of Hartshorne's work is followed by a discussion based upon Schloesing's work. The low vapor pressure of the water in wool of low condition (regain) indicates that the water is distributed in a molecular degree of fineness. With higher conditions, the vapor pressure increases, not merely absolutely but also relatively to the amount of water present, and at a condition far removed from saturation, the vapor pressure becomes nearly equal to that of pure water. Form this point onwards, the vapor pressure increases more and more slowly as saturation is approached. This last portion of the curve denotes a change in the nature of the absorption process to approximately a simple coarse-grained soaking up of water, such as occurs with a sponge. This gradual change is also shown by the evaporation of water from saturated wool. As the wool becomes drier the water is parted with less easily (even allowing for the diminished amount present), and the last water is removed with difficulty. The diminishing evolution of heat upon reconditioning dry wool also substantiates these data. Variations in the equilibrium condition of wool depend chiefly on the relative humidity and only slightly on the temperature of the air. The rate of change of wool towards equilibrium condition, whether gain or loss, depends upon the humidity and temperature of the air, the actual condition in the stock, and the form and nature of the stock. A high humidity and not too low a temperature are essential for rapid conditioning dry stock. Low condition in wool favors electrification of the fiber due to reduced condition. Increasing condition causes a decrease in tensile strength. If wet wool fiber under a state of strain due to an external force is dried, it will remain in approximately its strained position when the force is removed, the state of strain existing in a latent form. Upon wetting the fiber the strain again becomes externally active, but if the fiber is treated with boiling water or steam the strain is obliterated and cannot be revived by wetting.

See 368.

MOLECULAR WEIGHT.

345.—Molecular Weights of Proteins.

W. T. Astbury and H. J. Woods. *Nature 127,* 663-5 (1931). The possible arrangement of peptide chains in the structure of wool and hair is discussed. Svedberg has shown that the molecular weights of protein molecules are always 1, 2, 3 or 6, but never 4 or 5, times about 34,500. From this it is postulated that the protein may be built up of single peptide chains, pairs of chains pointed oppositely, threefold screws of chains pointing the same direction, or threefold screws of pairs of opposed chains, held together by secondary valences.

346.—Molecular Weight of Wool Protein.

H. vom Hove. *Melliand Textilber. 14,* 601-2 (1933). By measurement of the amount of halogen which combines with the tyrosine in wool when this is steeped for various periods in aqueous solutions of chlorine, bromine and iodine it is found (wool is assumed to contain 2.9 per cent of tyrosine) that the molecular weight of wool is 18,760. The data obtained indicate that mono- and di-halogenated tyrosines are formed with solutions containing 1.8 to 20.0 g of halogen per liter.

NITROGEN (See Chemical Constitution).

OXIDATION (See Halogenation).

347.—Studies Concerning the Reducing Power of Animal Fibers.

G. Ulrich. *Z. physiol. Chem. 55,* 25-41 (1908). The beneficial effect of formic acid in causing the fixation of chromic acid upon the fiber, was studied in detail with reference to the question whether the formic acid acted as the reducing agent. This was shown not to be the case. The effect was simply that of an acid partially hydrolyzing the fibers and thus allowing of the reducing action of the latter (cystine radicals) to become more potent in transforming the chromic acid to chromic oxide.

348.—Action of Ozone on Textile Fibers.

C. Doree. *J. Soc. Dyers Colourists 29,* 205-12 (1913). When wool is exposed to 2 per cent of ozone in an atmosphere kept saturated with moisture, its chemical and physical properties are only slightly affected.

349.—Spontaneous Combustion of Wool.

V. Lucchini. Milan. *Boll. chim. farm. 54,* 673-80; *Chem. Zentr. 87, I,* 1102 (1916). Spontaneous combustion of wool is due primarily to processes of auto-oxidation. In the presence of air and light the water content exercises a catalytic action on the fat of the wool and the fatty acids which are produced promote oxidation.

350.—Action of 30 Per Cent Hydrogen Peroxide (Perhydrol) on Cotton and Wool in Presence of Metallic Oxides.

R. Haller and J. Munk *Text. Forsch 4,* 138-4 (1922). Wool is rapidly attacked by 30 per cent hydrogen peroxide and yields a clear, non-opalescent solution which on evaporation to dryness by heating leaves a colorless, transparent laminated residue readily soluble in water, that neither gives the biuret reaction nor reacts with Millon's reagent. If the solution be allowed to evaporate to dryness at ordinary temperatures the residue gives no reaction with either sulfuric or thiosulfuric acid. In presence of a number of metallic oxides cotton immersed in hydrogen peroxide is unattacked, but wool is rapidly decomposed; this applies in particular to mercuric and aluminum hydroxides. In the presence of ferric, cobalt, zinc, cadmium, and tin hydroxides[3] the decomposition of wool is less rapid than that of cotton. Copper oxide causes very rapid decomposition of both substances; platinum and vanadium are without influence, while gold and palladium behave like copper.

351.—Investigation of the Reducing Properties of Wool.

R. Haller. *Helv. Chim. Acta 13,* 620-8 (1930). Contrary to general opinion, wool was not found a good reducing agent. No reducing influence could be detected when wool was treated with nitrates, dichromates, chromic acid, Fehling solution, indanthrene yellow R, or hydrogen peroxide. Slight reduction of ferric chloride was detected. Iodine was found quantitatively reduced. Sulfur was not found to be connected with the reducing properties of wool. Tables showing the influence of time and concentration on absorption of iodine by wool are included.

352.—Oxidation of Wool: Effect of Hydrogen Peroxide on Wool.

A. L. Smith and M. Harris. *Am. Dyestuff Reptr. 25,* 180-2P (1936); *Research NBS 16,* 301-307 (1936) RP875. The purpose of this investigation was to provide quantitative data showing the effect of oxidizing agents on wool as a basis for studying all processes in which wool is exposed to oxidation reactions. The work reported in this paper deals with the effect of hydrogen peroxide only. Data are presented showing the effects on wool of varying the concentration, temperature, and pH of the hydrogen peroxide solutions, and the duration of treatment. The main point of attack during oxidation is the disulfide group of the cystine in the wool. The extent to which the wool is oxidized bears a functional relationship to the decrease in the cystine content and to the increase in the alkali-solubility of the wool.

353.—Oxidation of Wool: The Lead Acetate Test for Hydrogen Peroxide Bleached Wool.

A. L. Smith and M. Harris. *Am. Dyestuff Reptr. 25,* 183-5P (1936); *Research NBS 16,* 309-313 (1936) RP876. The lead acetate test for distinguishing between untreated and hydrogen peroxide bleached wool has been investigated. The degree of darkening of the wool during lead acetate treatments is a function of pH, the maximum difference between untreated and bleached wool occurring at pH 5. The results indicate that hydrogen peroxide partially oxidizes the sulfur in wool and prevents the formation of lead sulfide. A mechanism by which lead sulfide is formed in untreated wool is described.

354.—Oxidation of Wool: Alkali-Solubility Test for Determining the Extent of Oxidation.

M. Harris and A. L. Smith. *Am. Dyestuff Reptr. 25,* 542-5P (1936); *Research NBS 17,* 577-583 (1936) RP928. Oxidizing agents attack the disulfide groups of the cystine in wool and increase the solubility of the wool in alkaline solutions. The determination of the alkali-solubility may be used as a measure of the extent to which the wool is oxidized. The method is applicable as a control in practical processes, such as bleaching and chlorination, and offers a measure of the extent to which wool is degraded by photochemical reactions. Data are presented which indicate a relationship between the chemical and physical degradation of wool fibers.

See 157, 231, 265, 292, 305, 306, 320.

REDUCTION.

355.—Hydrolysis of Wool by Sodium Sulfide, I.

W. Küster and W. Koppel. *Z. physiol. Chem. 171,* 114-55 (1927). In its hydrolyzing action on wool or hair sodium sulfide has a specific effect which cannot be accounted for by the sodium hydroxide formed according to the equation, $Na_2S + H_2O = NaSH + NaOH$. It undergoes successive oxidation and reduction, thus $Na_2S \rightarrow NaSH \rightleftharpoons Na_2S_x$, and at the same time the organic substrate is successively reduced and oxidized. Eventually, however, the sulfide becomes oxidized into sulfite, sulfate and thiosulfate at the expense of the organic matter. After 72 days' action of a 3 per cent solution of sodium sulfide on wool, the dialyzate was free from sulfide, and lead acetate gave only a white precipitate. As the wool dissolves, a part of it undergoes disintegration with formation of ammonia and diffusible nitrogeneous cleavage products, while the non-diffusible portion consists of the sodium salt of an insoluble acid residue, the acidity of which increases with the duration of the hydrolysis and the splitting off of ammonia. This residue amounts to nearly two-thirds of the original substance after five hours, and is somewhat greater at the end of 25 hours. After 125 hours the wool is completely dissolved, and the insoluble matter, present in the solution as the soluble sodium salt, is about one-half the original substance. Since the nitrogen content of the residual substance diminishes with the duration of the digestion, and increasing amounts of soluble and diffusible cleavage products are formed, it may be inferred that wool contains at least two proteins, A and B. One of these is more rapidly attacked than the other, so that after 125 hours' digestion A is converted into water-soluble products while B has undergone only minor changes. The basic amino acids are most readily broken off while the monoamino and dicarboxylic acids are more resistant. Of the two hypothetical proteins of the wool, the one which

goes into solution first (A) is probably richer in basic components. It probably contains, however, a nucleus which resembles in chemical constitution the more stable protein B. The insoluble residue differs from the original wool in its behavior when hydrolyzed by heating with water at 150°. The wool gave a higher pressure in the autoclave and a much smaller yield of amino acids and diketopiperazines. The residue after 125 hours' treatment with sodium sulfide, when hydrolyzed by hydrochloric acid and the products separated by the ester method, yielded glycerine, alanine, valine, leucine, aspartic acid, glutamic acid and proline, and a residue containing leucine anhydride.

356.—The Hydrolysis of Wool by Sodium Sulfide, II.

W. Küster and W. Irion. *Z. physiol. Chem. 184,* 225-40 (1929). In the hydrolysis of wool by 3 per cent sodium sulfide, one of the products formed is a non-dialyzable substance which can be precipitated by glacial acetic acid. It is a strongly acid protein derivative containing 12.8 per cent of nitrogen, and is resistant to further hydrolysis by sodium sulfide. Its low histidine content as compared with that of the original wool is not due to a destruction of histidine during hydrolysis, since histidine and various derivatives thereof are stable toward sodium sulfide. Likewise arginine, tyrosine and cystine yielded no ammonia when treated with sodium sulfide, but the amide nitrogen was split off quantitatively from asparagine. Hence the ammonia liberated from wool by sodium sulfide probably represents amide nitrogen. Cystine is undoubtedly the amino acid which is most susceptible to the action of sodium sulfide, since the sulfur bridge presents a conspicuous point of attack for the reducing agent. The keratin molecule is thus ruptured at each cystine linkage by an opening of the sulfur bridge and the formation of cysteine. The size of the fragments would depend on the distance between the cystine groupings in the peptide chain. The larger and less diffusible fragments should then have the lowest sulfur content. The acetic acid precipitate, however, contains more sulfur than the wool itself. This need not be surprising in view of the reactivity of the terminal cysteine, especially when oxidative influences are present. From the acid hydrolyzate of this acetic acid precipitate, no cystine could be isolated, and titration with iodine gave no evidence of cysteine. A crystalline substance was finally obtained which resembled cystine, but was more stable to potassium hydroxide, more reactive to potassium permanganate and contained only half as much sulfur. Analysis gave the formula. The substance evidently contains two carboxyl and two amino groups. It melts with decomposition at 275°, forms a crystalline hydrochloride salt, a methyl ester, hydrochloride and a crystalline copper salt. In attempting to prepare histidine peptides, a new derivative obtained was the azlactone of benzoylhistidine, m. 215°, by treatment of benzoylhistidine methyl ester with hydrazine hydrate.

357.—A Study of Keratin.

D. R. Goddard and L. Michaelis. *J. Biol. Chem. 106,* 605-614, (1934). Keratin dissolves in sodium sulfide, potassium cyanide, or thioglycolic acid at alkaline reaction. This effect is chiefly due to the splitting of the disulfide groups, which are essential for the maintenance of the fibrous structure of keratin. Chemically the action of thioglycolic acid is the simplest; it simply reduces the disulfide to sulfhydryl groups with no other appreciable chemical change. The other reagents act in a more complicated way. The substances thus obtained are proteins. They are soluble in alkali or acid, with a definite isoelectric point, and they are digestible by pepsin and trypsin, even when secondarily the sulfhydryl group has been reoxidized to the disulfide stage, or when, because of secondary reactions the sulfur content has been greatly changed.

358.—Derivatives of Keratin.

D. R. Goddard and L. Michaelis. *J. Biol. Chem. 112,* 361-370, (1935). The keratin of wool is reduced by sodium thioglycolate to kerateine. This can be oxidized to metakeratin, which differs from native keratin by its amorphous character, solubility in alkali, and by its digestibility with pepsin or trypsin. The hydrogen of the sulfhydryl group of kerateine was substituted by treatment with sodium iodoacetate, sodium α-bromopropionate, iodoacetamide, and iodoethyl alcohol. The derived proteins thus obtained differ distinctly in their solubilities and in their isoelectric points. They are all digested by pepsin or trypsin. No detectable substitution of amino hydrogen occurred during the treatment, and under proper treatment no loss of sulfur occurred. The derivative obtained with iodoacetic acid is soluble enough to allow the attempt of a fractionation with ammonium sulfate. This led to two fractions differing widely in solubility and sulfur content.

See 41, 322, 370.

SPECIFIC GRAVITY

359.—Specific Gravity of Wool and Its Relation to Swelling and Sorption in Water and Other Liquids.

A. T. King. *J. Textile Inst. 17,* T53-67 (1926). The topics considered are the effect of sorption on the actual determination of specific gravity, penetration by solvents and oils, influence of salts on swelling and sorption, and density methods of determining regain and of estimating wool-cotton mixtures.

SPECIFIC HEAT

360.—Specific Heats of Some Organic Substances.

G. Fleury. *Compt. rend. 130,* 437, (1900). The specific heat of dry wool is 0.393; of wool containing 11 per cent of moisture, 0.459.

STRUCTURE

361.—Internal Mechanics of Fibers Considered in Relation to General Colloid Theory and Technical Practice.

S. A. Shorter. *J. Soc. Dyers Colourists 41,* 207-16 (1925). The object of this paper is to formulate a general theory of fiber elasticity which will be of use in rendering comprehensible much of the complicated behavior of fibers in industry. The views put forward are founded on the recent work on the elastic properties of fibers and yarns.

362.—The Gel Structure of the Wool Fiber.

J. B. Speakman. *J. Textile Inst. 17,* T457-71 (1926). Contrary to Shorter's contention, Speakman found that the wool fiber possesses a true yield point in the sense that a fiber once extended is permanently more extensible at low tension. From a study of stress-strain diagrams, he developed a new theory of the gel structure of the wool fiber which accounts for its seemingly contradictory elastic properties, namely, a true yield point and perfect elasticity. According to this theory, the behavior of the wool fiber under stress is the behavior of a single cell, which consists essentially of three phases: (1) the elastic cell wall, enclosing (2) a fibrillar structure which is not in physical equilibrium with (3) a viscous phase of gelatinous character included in its interstices. The theory differs essentially from that of Shorter in its identification of two elastic phases, its recognition of a true yield point, its formulation of a different mechanism for adaptation to stress, and its explanation of the absence of structural recovery. Tables, diagrams and a sketch of the apparatus are given.

363.—Unscaled Fibers. A New Aspect of Fiber Research.

A. T. King. *Biochem. J. 21,* 434-6 (1927). A method has been devised for the me-

chanical removal of scales or outer layers of wool fibers in such a way as to leave the cortex or inner core intact for physical and chemical investigations. It consists essentially in drawing the fiber across the edge of a glass plate of suitable character.

364.—The Gel Structure of Wool Fiber.

S. A. Shorter. *J. Textile Inst. 18,* T78-80 (1927). Comment on paper by John B. Speakman (cf. Ref. 362). Reply. J. B. Speakman. *Ibid.* 80-1.

365.—Intracellular Structure of the Wool Fiber.

J. B. Speakman. *J. Textile Inst.* (*Special Issue 18,* T431-53 (1927). The elastic properties of the wool fiber as a whole are those of the single cell, which is assumed to consist of an elastic cell wall enclosing a fibrillar structure the interstices of which are filled with a viscous medium. This structure tends to lie preferentially along the axis of the fiber and is heterogeneous in composition. Under small stress, extension of the cell is at first delayed by internal friction, Hooke's law being obeyed up to 2 per cent extension for different wools in water and for the same wool at different humidities; for the same wool in water at higher temperatures (up to 100°), deviation begins between 1.4 and 2 per cent extension. Above this critical value rapid extension occurs chiefly by rotation of the fibrillae, the rate being determined by the viscosity of the medium within the cell and the elastic constituents of the cell framework; it is greatest at high humidities. When all the fibrillae are drawn into line, extension is retarded and afterwards takes place by direct extension of the fibrillae. The parts of the cell structure which are not plastic in water at ordinary temperatures become so at higher temperatures, while at 100° extended fibers take a set which is permanent as regards subsequent immersion in cold water and is due to plastic flow within the fibrillae. Different wools show fibrilla plasticity to different degrees, and for ease in manufacture wools should be highly plastic.

366.—The Rigidity of Wool and Its Change with Adsorption of Water Vapor.

J. B. Speakman. *Trans. Faraday Soc. 25,* 92-103 (1929). The rigidity of an English Cotswold wool was determined from the times of vibration of torsion bars suspended from fibers of known dimensions. Determinations were made at relative humidities from 0 to 100 per cent saturation at 25°. The rigidity of wool at any humidity between 23 and 87 per cent can be expressed by the formula: Relative rigidity = 1.255-0.047A. Absolute rigidity = 1.76 (1.255-0.047A) x 10^{10} dynes per square centimeter, where A is the amount of water adsorbed, expressed as percentage of dry weight. From the shape of the rigidity-water adsorbed curve, it is inferred that reduction in rigidity is caused by adsorption of water by certain groups in the wool molecule, but that water is adsorbed in two additional ways. The reduction in relative rigidity (R) with changing humidity (H) can be expressed by the formula: $R = 2.57 \times 10^{4} (H) + 1.78$.

367.—Elastic Properties of Wool in Organic Liquids.

J. B. Speakman. *Trans. Faraday Soc. 26,* 61-9 (1930). A general study of the solvation of wool by organic liquids. The plan is to determine the load-extension curves of single fibers of wool in organic liquids, the solvation of the fiber being deduced from the diagrams. The limiting size of the molecule capable of penetrating the dry fiber and modifying its elastic properties was determined from the elastic properties in a series of methyl, ethyl, propyl and butyl amyl alcohols, water serving as a reference. Reactions between alcohols and wool ceased when the molecule size exceeded that of propyl alcohol. The capillary spaces in the wool which must be penetrated to alter the elastic properties are therefore of the same order of size as the molecule of propyl alcohol. Observations were extended to include ethylene glycol, glycerol, nitrobenzene, nitromethane, acetone, pyridine, diethylamine and methyl cyanide. Organic reagents with hydroxyl groups in the molecule modify the elastic properties remarkably, provided the size of the molecule is small. In comparison, other reagents are strikingly inert. The mechanism of the reaction is a weakening of the lateral attraction between the micelles caused by the opening of the coordinate link, under the action of the hydroxyl-containing reagent.

368.—The Elastic Properties of Wool in Water at High Temperatures.

J. B. Speakman. *Trans. Faraday Soc. 25,* 169-76 (1929).

369.—Examination of the Fine Structure of Wool by X-Ray Analysts.

J. Ewles and J. B. Speakman. *Proc. Roy. Soc.* (*London*). *B105,* 600-7 (1930).

370.—Micelle Structure of the Wool Fiber.

J. B. Speakman. *Nature 126,* 565 (1930). The existence of micelles within the wool fiber was proved by swelling and adsorption studies and by the action of sodium sulfide on wool. It was deduced that the micelles are lamellar.

371.—X-Ray Investigations of the Inner Structure of Wool.

W. T. Astbury. *J. Textile Sci. 4,* 1-5 (1931). The minute structural elements of the wool fiber may be studied with the aid of X-rays. Wool is a complex biological structure built up from the protein keratin, which is characterized by containing sulfur in the molecule. The elements of the wool fiber are "to a large extent" crystalline, meaning that the constituent molecules are built together in a regular 3-dimensional pattern. Wool is generally called colloidal, but this is because its crystals are so minute. X-ray photographs are given, which show that stretched wool fibers have a different crystallographic structure from the unstretched; the latter is called α-keratin and the former β-keratin, though this difference is postulated entirely on the showing of the X-ray photographs and is not substantiated by any chemical analysis. Wool, when wetted, may be stretched to twice its normal length without losing its elasticity or its ability to regain its normal length when dried. But stretched wool is very susceptible to the action of steam, so that the β-keratin loses its power of returning to the α-form. The stretched wool is 20 times as sensitive to the action of sodium sulfide solution as the unstretched fiber. The X-ray measurements indicate that the α to β transformation is associated with a molecular elongation of from 5.15 to 10.2 A.U. along the axis of the fiber. Spatial molecular models are given showing a theoretical structure of the wool molecules.

372.—X-Ray Studies of the Structure of Hair, Wool and Related Fibers.

W. T. Astbury and A. Street. *Trans. Roy. Soc.* (*London*) *A230,* 75-101 (1931). Geelong 80's Merino wool, Australian 64's Merino wool, English Cotswold wool, human hair, llama hair, hedgehog spines, and porcupine quills were examined with monochromatic X-rays. The diffraction patterns indicate that the structures of all these substances are substantially the same, and undergo similar reversible changes on stretching. The α-pattern is prominent below 30 per cent extension and fades out at 60 per cent, being replaced by the β-pattern. These patterns are referred, provisionally, to rectangular cells of specified dimensions. The most prominent perodicity along the axis of the fibers is 5.15 A.U. (the same as in cellulose) in the α-form, and 6.64 A.U. in the β-form. The difference of 29 per cent is supposed to be connected with the marked change of elastic properties at 30 per cent extension. The β-form is more readily attacked chemically than the α-form. Suggestions are made as to the structural details of hair keratin.

A preliminary X-ray examination of cystine shows that the lattice is hexagonal with three molecules per cell and a = 9.40 A.U., c = 9.42 A.U.

373.—Micelle Structure of the Wool Fiber.

J. B. Speakman. *Proc. Roy. Soc.* (*London*) *A132* 167-9 (1931). The study of the elastic properties of wool in mixed solvents and the estimation of the work required to produce a given stretch allows the deduction that wool fibers are constructed of lamellar micelles. These are arranged with the long axes parallel to the length of the fiber and are some ten times as long as thick. The thickness of the micelles is of the order of 200 A.U. The intermicellar distance in dry fibers averages about 6 A.U. This space may increase in water to 41 A.U. This fact accounts for the increase of accessibility of wet wool to reagents of high molecular weight. The internal surface of wool was found to be approximately 1 by 10^6 sq. cm. g. Acids cause a destructive action on the micelles, free long-chain protein molecules and thus allow an extension of the fiber. The change is reversible and when the acid is removed the fibers reacquire their original properties. The attack of the micelles by acids proceeds from the same thin edges which were recorded with sodium sulfide solutions. (See 322.)

374.—Some Physicochemical Properties of the Wool Fiber.

J. B. Speakman. *J. Textile Sci. 4,* 6-9 (1931). This paper relates chiefly to the adsorption of dyes by wool. Dye molecules are so enormous that there would seem to be little chance of their ever entering the fiber. The size of the pores in the dry fiber were determined by reaction with alcohol hydroxyl groups associated with stretching of the wool, the work required to stretch the fiber being measured first in water, and then in methyl alcohol, ethyl alcohol, etc. The alcohols employed increased progressively in molecular size and weight. The resistance to extension increases until butyl alcohol is reached, when the fiber behaves as it does in dry air. Alcohols beyond butyl, therefore, do not enter the wool molecule, and therefore the size of the pores in the dry wool fiber is approximately the same as the length of the *n*-propyl alcohol molecule. The work required to stretch wool fibers 30 per cent (g.cm. per ml.) in various media at 22.2° is 5.37 x 10^5 for octyl alcohol and 1.63 x 10^5 for ethylene glycol. The increase of pore size of wool fibers swollen in water is more than 100 per cent. Dry wool fibers immersed in water give an increase in length of 1 per cent and an increase in diameter of 18 per cent. Water and other reagents are adsorbed on the surfaces of the constituent micelles, and cause a swelling of the fiber. Actual determinations of the pore size show that the micelles are about 200 *a.u.* thick. The size of the swollen pores is about 40 *a.u.* Thus any dye having a molecule greater than this size is only adsorbed on the exterior of the fiber and will be deficient in fastness to rubbing. On transferring the dry wool fiber from dry air to water the breaking load of the fiber is changed from 22.1 to 14.9 x10^5 g./cm.^{2}. The increase in cross-section is about 40 per cent and the rigidity is altered in the ratio of 15:1 as compared with the breaking load. This indicates that the micelles are much longer than they are thick. The conclusion is that the wool fiber is built up of tiny plates, 200 *a.u.* thick, the long axis of the plates being parallel to the length of the fiber. When the wool is swollen in water the distance separating the surfaces of the plates is about 40 *a.u.* whereas in the dry fiber this is only 6 *a.u.*

375.—The pH Stability Region of Insoluble Proteins.

J. B. Speakman and M. C. Hirst. *Nature 127,* 665-6 (1931). The pH stability range of wool keratin was determined by measuring the work required to stretch fibers 30 per cent of their length at 22.2° after 24 hours' soaking, first in a solution of pH 5.5, which is the middle of the stability range, then in solutions of other pH values. Wool was found stable between pH 4.0 and 7.0. The isoelectric point is 4.8. This is in harmony with Svedberg's work on soluble proteins, where it was found that each monodisperse protein has a fairly wide stability range, which includes its isoelectric point. Outside of the stability region the work required to stretch the fiber decreases; thus in 4.8 *N* hydrochloric acid 39 per cent less work is required. It is suggested that this is due to partial separation of the long-chain protein molecules which form the micelles.

376.—Molecular Structure of Textile Fibers.

W. T. Astbury and H. J. Woods. *J. Textile Inst., 23,* 17-34T (1932). Recent work on the structure of textile fibers, rubber, chitin, asbestos, etc., is discussed and a general theory of fiber structure based chiefly on the x-ray data is put forward. Fibers may consist of fully extended chain molecules, *e.g.,* cellulose, natural silk, stretched wool, hair and rubber, or of folded molecules, *e.g.,* unstretched hair and rubber. The extended-chain molecules are almost non-elastic, and fibers built from them extend by internal slipping; but folded molecules may unfold and pass into the extended state, thus giving a long-range elasticity to fibers composed of them. In stretching the "fixed" fibers the inter-crystalline linkings give way before the intra-crystalline linkings, while with "folded" fibers the converse holds. The fibrous material from feathers represents an intermediate stage, between the "fixed" and "folded" fibers. Typical stress-strain diagrams of various fibers, and supercontraction of fixed fibers, *e.g.,* natural silk, are also discussed.

377.—X-Ray Interpretation of Fiber Structure.

W. T. Astbury. *J. Soc. Dyer Colourists 49,* 168-79 (1933). X-ray microscopical studies show that all textile fibers have a certain similarity of structure. The molecules of all are aggregated into crystalline or pseudo-crystalline groups (micelles). These aggregates are formed of long, thin fiber molecules which lie with their long axis roughly parallel to the fiber (ramie, silk) or are arranged so as to form a spiral around the fiber axis (cotton. The molecular aggregates are held together by virtue of residual molecular attractions which may be reenforced by orthodox chemical side chains. The strength of the natural fibers is ascribed chiefly to the great length of the molecular chains. The intermicellar spaces in the fibers are enormous compared to the size of the micelles. The elastic and stretching characteristics of wool are believed due to the fact that the wool polypeptide molecule is folded and held fixed by side chains. In water the attractions of the side chains are reduced and the wool fiber can be extended. During drying the side chains reunite with each other and the wool regains its original dimension. Silk and cotton molecules do not possess a folded condition in the fiber.

378.—X-Ray Studies of the Structure of Hair, Wool and Related Fibers, II. The Molecular Structure and Elastic Properties of Hair Keratin.

W. T. Astbury and H. J. Woods. *Trans. Roy. Soc.* (*London*) *A232,* 333-94 (1933). About 200 x-ray photographs of mammalian hairs, spines, etc., were taken under a great variety of conditions. The x-ray fiber photograph of stretched hair (β-Keratin) is analogous to that of natural silk (fibroin), whether stretched or unstretched. Stretched hair is therefore built of extended polypeptide chains, while unstretched haid (α-keratin) must consist of the same chains in a folded state, so that the elastic mechanism is that of a reversible intramolecular transformation. By means of "quadrant photographs" it is shown that the molecular complex of

α-keratin stretches reversibly by about 2 per cent before the onset of the main transformation. The limiting elastic extensibility of all mammalian hairs is about 100 per cent of their initial unstretched length. Intramolecular folds (transverse to the general direction of the side chains) of the nature of linked pseudodiketopiperazine rings, which open up on extension to produce the normal zigzag protein chain, are assigned to α-keratin. The side chains of β-keratin are roughly coplanar and serve to unite neighboring main chains by a variety of cross linkages, including both covalent and electrovalent bonds. In the extended configuration the existence of the "primary fold" in the main chains reduces the average length of an amino acid residue to less than is found in fibroin. The structure of β-keratin is one of flat polypeptide "grids" adhering by virtue of attractions between carboxyl and imido groups. The normal equilibrium form of these grids involves the transverse "secondary folds." The general intramolecular elastic mechanism of keratin thus falls into line with that of simple molecules, though the usual main chains and side chains, and by the longitudinal attractions between electropositive and electronegative centers in the latter. The available chemical analyses of keratin are in close agreement with the concept of an average volume per amino acid residue of 3.38 x 4.65 x 9.8 *a.u.*, as deduced from average length of the residue, the thickness transverse to the side chains and the average width in the plane of the side chains. These quantities may be used to calculate the average diameter of all proteins and the average thickness of monomolecular protein films. An approximate tentative scheme for the distribution of the keratin side chains is proposed. The elastic properties of hair are referred to three "phases," intercellular, cell-wall, and intracellular keratin, which, respectively, show increasing powers of resistance to extension and the action of reagents, and function elastically both in series and in parallel. The phenomena exhibited under the following conditions are studied and explained: stress of water at increasing temperatures, action of dilute sodium hydroxide at ordinary temperature, adsorption of water, hydrolysis with steam or dilute alkali, irradiation with ultraviolet light or x-rays, and action of potassium dichromate and of eosin.

379.—Constitution of the Keratin Molecule.

J. B. Speakman and M. C. Hirst. *Trans. Faraday Soc. 29,* 148-72 (1933). The micelles of the wool fiber consist of long peptide chains bridged across by salt linkages on the one hand and cystine on the other, the salt linkages being formed from glutamic or aspartic acid and arginine, lysine or histidine. Other types of linkage must exist.

380.—X-Ray Studies of the Structure of Hair, Wool and Related Fibers, III. The Configuration of the Keratin Molecule and Its Orientation in the Biological Cell.

W. T. Astbury and W. A. Sisson. *Proc. Roy. Soc. (London) A150,* 533-51 (1935). When pressed in steam or hot water, α-keratin fibers are transformed to β-keratin, the crystallites of which rotate about their long axes, bringing the protein chains parallel to the pressure. Direct determinations show that the "backbone" and "side-chain" spacings of the keratin "grid" are mutually perpendicular. The crystallites of β-keratin are broader in the direction of the "backbone" spacing than in that of the "side-chain" spacing. The biological cells in keratinous structures are generally flat and arranged with their flat sides approximately parallel to the natural surfaces of the specimen. The protein side chains are not naturally perpendicular to the cell wall; selective orientation under pressure is thus not simply a consequence of cross-sectional deformation. Within the cell the keratin grids are randomly oriented about the fiber axis. The orientation phenomena are explained in terms of the flat crystallites and the action of steam on the cross-linkages of the keratin grid. The mechanism of the evolution of fibrous proteins is discussed with reference to the results obtained from x-ray studies of other proteins.

381.—Dichroism of Dyed and Stretched Wool Fibers and Its Use in Revealing Structure.

D. R. Morey. *Textile Research 5,* 538-41 (1935).

382.—X-Ray Study of Protein Fibers.

W. T. Astbury. *Textile Mfr. 62,* 236 (1936); *Textile Recorder 54,* 36, 35 (1936). By the means of x-ray applications specially adapted to the purpose, it is shown that when tension is applied to the grid, the fibers stretch continuously and reversibly over a range of about 2 per cent and after that a transformation takes place. The discovery establishes the structural link between the obviously fibrous proteins and the wide regions of apparently nonfibrous proteins.

383.—The Separation of Wool Into Its Histological Components.

R. Haller and F. W. Holl. *Kolloid-Z. 75,* 212-17 (1936). The wool is separated into its histological components, cortical cells, scale cells, and cementing material, by means of concentrated ammonia. A sulfur-free protein, named "lanain," was obtained from the cementing material. The denatured "lanain" redissolves in concentrated ammonia and it can be precipitated again from this solution. This, therefore, gives a method for the regeneration of denatured proteins. An unknown crystalline substance, insoluble in water, alcohol, and ether, m. 110°, was isolated from the wool. The use of concentrated ammonia for the decomposition of dyed wool was not successful.

384.—Cross Linkage Formation in Keratins.

J. B. Speakman. *Nature 138,* 327 (1936). New linkages formed in the setting of stretched fibers of wool in the strain are probably of the -S-NH- type and not of the type -N=CH-.

See 72, 77, 228.

SULFUR (See Chemical Constitution).
SWELLING.

385.—The Effect of Neutral Salts in Retarding the Swelling of Fibers in Acid or Alkaline Solutions.

M. H. Fischer and G. Moore. Oakland, Calif. *Z. Chem. Ind. Kolloide 5,* 197-9 (1909). Equimolar salt solutions do not show equal effects in retarding the swelling of fibers in acid or alkaline solutions. The retarding action of any salt on the swelling of fibers in any acid or basic solution is roughly proportional to the sum of the constituent ions. In order of increasing retardation of the swelling effect the anions are chloride, bromide, nitrate, thiocyanate, iodid, acetate, sulfate, phosphate, tartrate and citrate; the cations, potassium, sodium, ammonium, magnesium, calcium, copper, iron.

386.—Properties of Wool.

L. Meunier and G. Rey. *Cuir. Tech. 16,* 530-6 (1927). Previous results on the action of ultraviolet light on wool are amplified. By means of swelling experiments in buffered solutions the isoelectric point of wool was shown to lie at pH 3.6 to 3.8. The complete swelling curve from pH —0.5 to pH 10.0 has now been obtained in solutions of hydrochloric acid and sodium hydroxide, free from buffer salts. The minimum corresponding to the isoelectric point lies at pH 4.0 to 4.5. The acid swelling rises to a maximum at pH 1.0 to 1.5, falls to a minimum at pH 0, and rises sharply again in very acid solution. The swelling in alkalies increases continuously up to pH 10.0, with a point of inflection at pH 7.5. Experiments with salt solutions at pH 5 to 7 indicate that sodium salts exert a specific swelling effect, the order being roughly that of the Hofmeister series. Reducing the basic character of the wool, by deamination or treatment with quinone, greatly reduces the acid swelling. By deamination the isoelectric point is shifted approximately 0.5

pH unit to the acid side. By chlorination, irradiation, or pretreatment with hydrogen sulfide solution, the alkaline swelling is increased, which is attributed to increased reactivity towards hydroxyl. By a modified Van Slyke method, wool is shown to contain about 0.57 per cent nitrogen as primary amino nitrogen.

387.—Properties of Wool.

L. Meunier and G. Rey. *Halle aux cuirs, 138-48* (1929). The swelling of wool is a function of pH value. A study was made of the effect of sales on swelling. Hanks of degreased wool were immersed for 48 hours at 18 to 20° in normal solutions of salts, then centrifuged and weighed. The gain in weight was taken as the measure of swelling. Results for sodium salts were: sodium iodide, 5.9 per cent; sodium thiocyanate, 56.4 per cent; sodium bromate, 52 per cent; sodium nitrate, 52 per cent; sodium chlorate, 51 per cent; sodium chloride, 48 per cent; sodium acetate, 47 per cent; sodium sulfate, 46 per cent; sodium citrate, 46 per cent; water, 45 per cent. The pH values of these solutions all lay between 5.2 and 7.2, and there was no relation between pH value and degree of swelling. High concentrations of sodium thiocyanate at high temperatures peptize wool to give strongly fluorescent solutions. The swelling curve of wool in acids and alkalies was obtained with solutions of sodium hydroxide and hydrochloric acid, free from salts. The curve shows a sharp minimum at pH 0, a sharp maximum at pH 1.25, a broad minimum at pH 3.75 to 5.25, and an apparent inflection point at pH 8. Deaminized wool, and wool treated with quinone, swell less than ordinary wool in pH range 0.5 to 3, and the isoelectric point is displaced toward pH 3. Irradiated wool swells more at all pH values than ordinary wool, but the isoelectric point is unchanged. In solutions of hydrogen sulfide, wool swells less than in pure water, but wool pretreated with hydrogen sulfide swells more in alkaline solution than does wool not pretreated. This supports the hypothesis that sulfhydroxyl renders keratin more reactive toward hydroxyl. For the determination of amino groups in wool, the apparatus consists of (1) a source of carbon dioxide and a purification train, (2) a reaction vessel consisting of glass-stoppered flask provided with gas inlet and outlet, and stopcock thistle tube for introducing acid, (3) an absorption bottle containing a solution of 20 per cent sodium hydroxide and 6 per cent potassium permanganate, and (4) a gas-measuring tube (1 g wool is placed in the reaction flask). The apparatus is freed from air by a current of carbon dioxide. A mixture of 20 ml of 10 per cent sodium nitrite solution and 15 ml of glacial acetic acid is introduced through a stopcock funnel. Reaction begins immediately. Nitrogen dioxide and nitrogen are evolved and entrained by the current of carbon dioxide. Carbon dioxide and nitrogen dioxide are absorbed by alkaline potassium permanganate. The nitrogen is collected and measured. A sample of raw, degreased wool gave 0.57 per cent nitrogen. Chemical treatment that tends to hydrolyze wool increases the yield of amino of nitrogen. Silk fibroin gave only 0.40 per cent of nitrogen, which indicates fewer amino groups than in wool. This is in line with the greater swelling of the latter.

388.—Swelling of Wool Fibers in Water and in Aqueous Solutions of Sodium Hydroxide as Shown by the Change in Cross-Sectional Area.

M. H. Norris. *Trans. Faraday Soc. 28,* Pt. 8, 618-26 (1932). An apparatus (described) was made so that the fiber could be centrally located in the solution, prevented from twisting by a light Pt. sinker, and its diameter measured microscopically at definite points, and also the diameter at one height measured as the fiber was rotated. When the fibers were subjected to a cycle of sodium hydroxide solutions, from 0.01 to 0.125 *N* and back as the concentration of sodium hydroxide increased, the percentage swelling steadily increased, but as the concentration of sodium hydroxide decreased the diameter remained practically constant (at a high value for 0.125 *N* sodium hydroxide) until about 0.025 *N* sodium hydroxide was reached, after which it decreased but not to its original value. Badly damaged fibers continued to swell in 0.05 *N* sodium hydroxide until they finally broke. The behavior of the fibers is explained by the postulation (supported by communicated x-ray data) that water enters only between the micelles, while sodium hydroxide penetrates the micelles; thus, after a fiber has once been treated with sodium hydroxide, water can also enter the micelles, while glycerol dehydrates the fiber whether it is damaged or not. Stretched fibers swell appreciably more than unstretched ones. This is in keeping with Astbury's x-ray findings that the extended protein chain (β-keratin) is more vulnerable than the normal folded chains of α-keratin. No change was found in the cross-sectional shape of the wool fibers during swelling or subsequent shrinking.

389.—Swelling of Protein Fibers, III. Horsehair.

D. J. Lloyd and R. H. Marriott. *Trans. Faraday Soc. 30,* 944-58 (1934). Horsehair was subjected to solutions in which pH varied from 0.3 to 13. Oxidizing, reducing, and hydrating agents, hydrogen peroxide, potassium persulfate, sodium sulfide, lithium iodide, sodium chloride, sodium acetate, thiourea were added. Changes in weight, diameter, length, birefringence, and tendency to split into spindles were observed. The data recorded in four tables and one graph indicate that: (1) Keratin fibers absorb about 28 per cent of their dry weight of water from pure water and many aqueous solutions. (2) If untreated, this absorption is not due to a Donnan equilibrium. (3) Preliminary treatment with sodium hydroxide causes greater swellings. It seems irreversibly to open coordinate links between carboxyl groups and imido groups on different chains and peptide links. These opened linkages permit the binding of water molecules. Donnan equilibrium conditions also arise. (4) Preliminary treatment with 4 *N* hydrochloric acid does not lead to subsequent swelling or development of a Donnan equilibrium on treatment with acid or base. The linkages are reversibly opened by hydrochloric acid. (5) Birefringence is little affected by acid solutions up to 5 *N*. Increase of acid concentrations above 5 *N* causes a rapid fall, leading to total extinction at 11.4 *N* hydrochloric acid. Washing out the acid does not restore birefringence. (6) In increasing concentrations of alkaline solutions birefringence irreversibly disappears at about 1 *N*. (7) In alkaline solutions, oxidizing agents cause swelling accompanied by increase in length up to 30 per cent. (8) In acid solutions, oxidizing agents produce no swelling, but cause contractions up to 15 per cent in length. (9) In alkaline solutions reducing agents produce swelling and elongations up to 50 per cent in length, and total irreversible loss of birefringence. (10) In acid solutions reducing agents have no effect. (11) x-ray examinations show some loss of definition but no fundamental changes in structure caused by treatment with acid, alkali, or sulfide. (12) Hydrating salts have mainly intermicellary effect, swelling without affecting birefringence. The keratin molecules are in the α form and are closely packed in parallel orientation and held with strong collateral forces. Imbibitional swelling occurs without disturbing these forces and it may be reversed. When these forces are disturbed, molecules may be reoriented, crystalline character lost, hydration at charged centers occur, and a Donnan equilibrium develop. These changes are irreversible and affect the packing of the molecules but do not change α-keratin to β-keratin.

See 15, 253, 255, 262, 285, 304, 374.

TANNING (See Mordanting).

See 285, 291, 292, 310, 311, 318, 386, 387.

X-RAY (See Structure).

The Keratin Fibers

*A Communication to the Research Committee of the A. A. T. C. C.**

WM. HARRISON, M.Sc. Tech. Manchester, M.Sc. Leeds, F.I.C., F.T.I.

WITHIN the last twenty years a considerable amount of work has been carried out upon the Keratin fibers: hair, wool and silk, with a view to determining their physical and chemical structure. The X-ray methods utilized so effectively in solving the structure of many organic crystals have been made use of in the examination of the Keratin fibers[1]. The X-ray spectra of hair and wool are much less defined than those of most organic crystals; they are in fact less defined than the spectrum of native cellulose as present in ramie or of the fibroin present in natural silk. Nevertheless the X-ray spectra indicate crystalline structure however imperfect and making due allowance for the diffusion and overlapping of the spots in the X-ray spectrum photographs it is possible to calculate the probable shape of the crystals and to learn the likely special arrangements of atoms in the crystals.

***We are pleased to receive for publication the accompanying communication. Mr. W. Harrison of Scotland has made a wide study of Keratin fibers and during the past few years has followed with interest the work of our research associate, Dr. Milton Harris, on the Chemistry of Wool. We believe that this article will be of considerable interest to all who are interested in the chemistry of the animal fibers.—L. A. O.**

The problem is, however, much complicated by the fact that these Keratin fibers are not homogeneous. The cortex or interior portions of the fibers show definite fibrillar structure in the microscope whereas the cuticle shows no such structure, it appears as a very fine network structure. When Keratin fibers are treated with a 1 per cent solution of sodium sulfide the inner portions become dissolved out while the cuticle remains as a hollow tube which can easily be split. The portions dissolved out by the sodium sulfide appear under dark ground illumination to consist of fine elongated particles suspended in a clear liquid. The cuticle differs from the remainder of the Keratin fiber in offering a much greater resistance to the action of sodium sulfide and in fact to the action of many other reagents and in possessing a different microscopic structure. The X-ray spectrum of the cuticle, especially in the stretched condition differs from that of the whole fiber[2] hence when the cuticle is partially removed from the hair and wool the X-ray spectrum becomes more sharply defined[3]. It is however not possible to remove the cuticle completely from the fibers or to free the cuticle from attached cortical substances, hence it is impossible to say how much the X-ray spectrum of one constituent interferes with that of another. In the case of cotton fibers it has been shown[4] that the absence of the characteristic spectrum of cellulose in the fibers before approximately 30 days' of growth is due to the interference of other substances of similar composition.

In the case of the Keratin fibers some of the more diffuse and weak spots may be partly dependent on the cuticle. When hair and wool are stretched 30 per cent or more the X-ray spectrum is changed[5] and becomes similar in some respects to the X-ray spectrum of silk fibroin but the spots on the photograph are much more diffused than those on the photograph of the spectrum of fibroin. The important point of similarity is regarded as that between the spots due to reflection from lengthways spacing in the stretched hair and fibroin, respectively. Thus, in the spectrum of fibroin there appear spots representing spacings which are multiples of 3.5 Ångstrom Units while in the spectrum of stretched hair there appear spots representing spacing which are multiples of approximately 3.4 Ångstrom Units. This form of Keratin present in stretched hair has been termed beta Keratin while the form present in normal and unstretched hair has been termed alpha Keratin. The similarity in the spacings in stretched hair and wool and in natural silk is regarded as indicating some definite similarity in chemical structure.

The X-ray spectrum of the alpha Keratin in normal hair and wool is in agreement with that of a rectangular unit cell of dimensions a = 27 ± 2 Å U, b = 10.3 Å U, c = 9.8 Å U. The strongest reflections correspond to spacings of 5.15 Å U (020), 7.93 to 9.8 Å U (201,300,101,-001) and 27 ± 2 Å U (100). The X-ray spectrum of the beta Keratin in stretched hair and wool indicates that the symmetry of the crystal corresponds to that of a rectangular unit cell of dimensions a = 9.3 Å U, b = 6.64 Å U, c = 9.8 Å U. The strongest reflections correspond to spacings of 4.65 Å U (020); 3.32 Å U (020); 9.8 Å U (001) and 3.75 Å U (210).

The X-ray spectrum of fibroin according to Herzog and Kratky[6] corresponds to that of a monoclinic cell. a = 9.68 Å U, b = 7.00 Å U, c = 8.80 Å U angle $\beta = 75° 50'$.

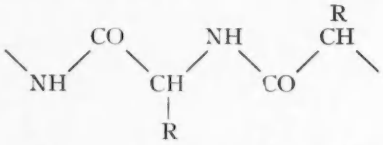
The spacing 020 of 3.5 Ångstrom Units is the one arranged lengthways to the silk fiber.

The polypeptides of Keratin fibers are regarded as belonging to the type —NH—CO—CH—. The length
R
of such a unit has been calculated to be of the order of 3½ Ångstrom Units[7]. To make this calculation the following dimensions were assumed:

Distance between carbon and carbon	C — C, 1.54 Å U
Distance between carbon and nitrogen	C — N, 1.32 Å U
Distance between carbon and oxygen	C = O, 1.15 Å U
Distance between nitrogen and hydrogen	N — H, 1.08 Å U

There is some uncertainty about the distance between carbon and nitrogen as it varies in different compounds. Thus in methyl azide it is 1.47 Å U, in hexamethyl tetramine 1.44 Å U, in urea 1.33 Å U and in thiourea 1.35 Å U, in fact atomic spacings of all kinds vary considerably between different compounds. The calculations must, therefore, be regarded as approximate so that the X-ray spectra cannot be taken as proof of the chemical constitutional formula proposed.

Astbury and Woods[8] regarded this calculated spacing of 3½ Ångstrom Units to be sufficiently near the 3.32 Ångstrom Unit spacing observed in B Keratin to be sufficient justification to adopt the constitutional formula



for the polypeptide molecules oriented lengthways along the fibers of silk and of stretched hair and wool.

Since the change from alpha to beta Keratin can be produced by stretching the fibers of hair and wool these authors concluded that the lengthways spacing of 5.15 Å U in alpha Keratin became extended to some multiple of 3.32 Å U in the beta Keratin.

In making the first selection of a change from 5.15 Å U to 2 × 3.32 Å U Astbury and Woods[9] took into account the following observations:

1. That the readily distinguishable reflections in the beta photograph lie on hyperbolae corresponding to a period along the fiber axis of about 6.7 Å U which is some 30 per cent greater than the spacing 5.15 Å U of the prominent meridian in the alpha photograph.

2. That the well marked "shoulder" of the normal load-extension curve and the first appearance of the B photograph both occur in the neighborhood of 20-30 per cent.

3. That permanent damage of the fiber structure as measured by Speakman[10] is inappreciable for quick extensions of less than 30 per cent.

4. That the density of stretched hair and wool is approximately the same as that of normal hair and wool.

5. That the highest true "permanent set" which may be obtained with wool in practice is approximately 29 per cent.

Based on the above observations the following statements were made:—

"The alpha beta transformation is reversible and appears to be based on the elongation of an intramolecular group of length 5.15 Å U to another group of length 6.64 Å U, an increase of 29 per cent."[11]

"If we are justified in attaching any significance to these dimensions then it ought to be possible to link them up with the reversible transformation which exists between the alpha and beta forms. Assuming that the density of stretched hair is not very different from that of unstretched hair then the volumes of the two pseudo cells should be the same. As a matter of fact the spot of spacing 4.65 Å U which we have chosen as (200) of the beta form be taken as (400) this relation is indeed roughly true for $\frac{18.6 \times 9.8 \times 6.64}{9.5 \times 5.15} = 24$ Å U which is sufficiently near to the 27 ± 2 Å U mentioned above when it is recalled that the spot of this estimated dimension is in reality spread over several Ångstrom Units and it is too near the center spot to be measured with accuracy."[12]

Thus, in the early stages of this X-ray investigation the idea of molecular chains having an extensibility of about 30 per cent was considered to fit in with X-ray observations, with density measurements and with observations upon the elastic properties and the elastic breakdown of Keratin fibers.

Before this paper was issued these authors changed their views. Thus on pages 100-101 of the same journal[13] there appears the following statement:—

"We have been able to show that by suitable treatment with steam the load-extension curve of hair may be permanently smoothed out and the elasticity of form may be demonstrated in cold water over a range of from —30 per cent to about +100 per cent. The whole fiber then behaves as an elastic chain whose length can be almost doubled without rupture occurring. Without entering into a full discussion we may say that the observation strongly suggests that the full alpha to beta transformation of hair is accompanied by an elongation of the Keratin complex of approximately 100 per cent and that some relation on this basis must exist between the respective dimensions and features of the alpha and beta photographs. If now we assume that the two strong meridian reflections 5.15 Å U and 3.32 Å U that characterize the reversible transformation are linked by the relation 5.15 ⇌ (3 × 3.22). We have at once a quantitative explanation of the maximum extension and also the clue to the nature of the Keratin chain."

In order to justify this change of opinion the following remarks were made:—[14]

"Argument (1) is invalidated by the realization that the true unit of pattern is probably very large and that there is a simple general explanation of the occurrence of both the period 6.7 Å U and that of half this spacing.

Argument (2) cannot hold now that it is shown that there is a variety of restricted load-extension curves but

only one generalized curve *even though the progress of the intramolecular transformation as revealed by the X-ray photographs is very much the same in all cases.*

Argument (3) also now takes on a more general explanation.

(4) No reference to density is made.

(5) The evidence of permanent set is not mentioned in this connection.

In reference to the points (1) to (5) just discussed the present writer makes the following comments:—

(1) If the true unit of pattern is very large it offers so many possibilities that it becomes impossible to justify any selection.

(2) Since the same change in X-ray spectrum occurs in all cases it cannot be dependent on the nature of the load-extension curve.

(3) Since it has been proved that permanent damage to the structure occurs after the extension exceeds 30 per cent the generalized load extension curve must apply to fibers with damaged structure and may have no connection with the changes in X-ray spectra.

(4) In so far that the new dimensions selected for the hypothetical molecular chains necessitates a reduction in density of the unit crystals of about 25 per cent when the chains are stretched 100 per cent there must be present in the fiber some other constituent which increases its density. There is no evidence of this effect.

(5) The case of permanent set will be considered later in this paper.

Before one can accept even tentatively the idea that in alpha Keratin there are present folded molecular chains composed of sections 5.15 Å U long which in beta Keratin are extended to 10.3 Å U one must make sure that the 100 per cent extensibility of Keratin fibers is conclusively associated with the change in X-ray spectrum, it being unreasonable to associate the dimensional changes of the complete fibers with the changes in X-ray spectrums of that small fraction which is crystalline.

Firstly with a smooth load-extension curve one would expect a gradual increase from 5.15 Å U to 10.3 Å U in the spacing as the fiber is stretched. Thus[15] there appears the following statement:—

"The spacing of the strong arc on the meridian of the alpha photograph was originally given as 5.15 Å U but we have now been able to show that this is a maximum value arising out of the fact that it is almost impossible to build up a bundle of straight parallel hairs without stretching them slightly. The true 'unstretched' spacing is about 5.06 Å U as determined from small pieces of porcupine quill, etc."

If this statement of Astbury's is accepted then his own theory of extensible molecular chains requires a gradual change from 5.15 Å U to 10.3 Å U to be observed by X-rays.

Secondly, the change from alpha to beta Keratin must always occur when hair is stretched and the 100 per cent extension must be needed to complete the change; the reverse change must always occur when the fibers shrink back to normal length.

Thirdly, it should not be possible to convert alpha to beta Keratin without stretching the fibers.

More recent work has shown quite conclusively that none of these conditions actually exist.

Firstly: There is no gradual change from 5.15 Å U to 10.3 Å U, one finds in the X-ray spectra of hair multiples of 5.15 Å U and multiples of 3.32 Å U according to whether the Keratin is alpha or beta. Because of this Astbury and Woods had to adopt "the general idea of the sudden and at first rapid unfolding of molecular chains, etc." Yet[17] they refer to "The continuous variation in length and linkage of the side chains." These side chains are assumed to exercise control upon the main chains and should show continuous variation only if the main chains vary continuously.

Secondly: It is possible by treating hairs with boiling sodium bi-sulfite to change them in such a way that no change in the form of the X-ray spectrum occurs when the fibers are stretched or released after stretching.

Thirdly: It is possible to convert the alpha Keratin into beta Keratin by lateral compression[18] in which some extension occurs to a lesser degree than 30 per cent. It is possible to convert the alpha Keratin into beta Keratin by boiling hair in 5 per cent sodium bi-sulfite without causing any increase in length; in fact, the length can either be retained or cause to become less[19] according to the way in which the treated fibers are dehydrated and the Keratin remains in the beta form (see also ref. 20). All these facts prove quite conclusively that the change from one crystal symmetry to another is not in any way related to the elasticity of Keratin fibers; it is an entirely independent phenomenon. The fact that the dimensions 5.15 Å U and 3.32 Å U are, within experimental error, in the simple ratio 3 to 2 gives a very important clue to the real nature of the change from alpha to beta Keratin which will be dealt with in a later part of this paper. The fact that the X-ray photographs of all natural protein fibers such as animal hairs, muscle, collagen, feather, etc., show certain features in common[21] merely shows that they tend to crystallize in one of two forms and that there is some similarity in molecular configuration.

The fact that all these natural fibers are elastic is an entirely different matter from crystalline structure, the elasticity is, in fact, more likely to be controlled by the major non-crystalline portions and is observable under conditions when no change in crystalline form occurs.

The fact that certain proteins in the natural state change their crystalline form on "denaturation"[21, 22] provides no evidence of the true nature of that change in form. The same applies to the fact that similar changes in crystalline form can be produced in cortical cells from disintegrated Keratin fibers[21]. With such inconclusive evidence it is

unreasonable to proceed to postulate extensible and contractile molecular chains in all proteins.

The fact that fully stretched rubber gives a distinct X-ray spectrum indicates some regular arrangement of atoms or molecules but provides no evidence of what happens when the rubber is allowed to contract. It was suggested many years ago but not proved that the long rubber molecules form into coils. It is very unlikely that the isoprene units in these long molecules fold upon themselves in single units and inconceivable that the isoprene units themselves fold up but it is something of that order which Astbury assumes to take place in Keratins. Rubber itself has volumetric elasticity, it can be stretched in all directions, it therefore shows the properties of a liquid in a restricted form, the formation of crystals when that "liquid phase" is frozen[21] is only to be expected and does not prove that freezing causes coiled rubber molecules to uncoil.

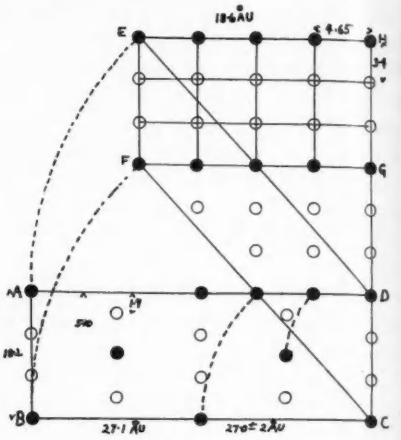
While the idea of coiled long chain molecules is attractive we have no evidence in proof of it. Coiling may take place but if it does the angle of bend at the junctions between isoprene units is, after 100 per cent elongation, likely to be small and many times smaller than is needed for Astbury's hypothesis concerning Keratin. In any case rubber is an entirely different substance from the proteins and shows only one X-ray spectrum and exhibits elasticity without need for the presence of a solvent so that one cannot argue by analogy between rubber and proteins.

From the arguments raised it is clear that the existence of two forms of Keratin as observed by X-rays has no direct bearing upon the elastic or other properties of the Keratins. We must, therefore, discard the hypothesis of extensible and contractile molecular chains having the property of folding at atomic distances and seek some other explanation of the observed facts.

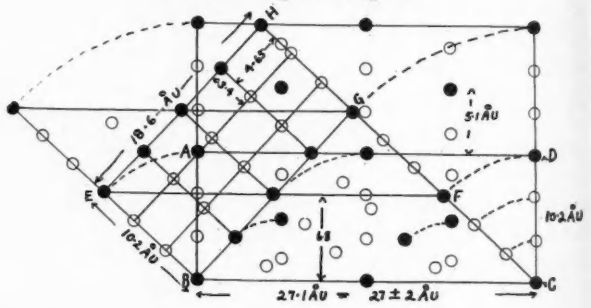
ALPHA AND BETA KERATIN

The X-ray spectrum of alpha Keratin present in normal hair and wool indicates that there are lengthways spacings which are multiples of approximately 5.1 Å U while that of the beta Keratin present in hair and wool after treatment in various ways indicates lengthways spacings which are multiples of 3.4 Å U. The fact that these spacings are in simple proportion bears much significance in crystallography where such simple relationships are so frequently met with. Because of this it seems likely that the two forms of crystal alpha and beta Keratin are simple geometrical derivatives of one another. If one takes the dimensions given by Astbury and Street[23] for the unit crystal of alpha Keratin and considers what would happen if the rectangular cell were deformed into a monoclinic cell of the same length of sides and this deformation continued until the atoms or groups of atoms which lie in the planes spaced 5.1 Å U apart again lie in planes one finds that the new planes must be spaced at 3.4 Å U apart. The exact conditions are seen in Diagrams 1 and 2.

RIGHT—
Fig. 1—Diagram 1.



BELOW—Fig. 2—Diagram 2.



In Diagram 1, ABCD represents the rectangular unit cell of dimensions 27 ± 2 Å U × 10.2 Å U × 9.8 Å U, CDEF represents the monoclinic cell form when the atoms A and B are moved with respect to C and D to new positions E and F, such as might occur if the whole structure were elongated. This monoclinic cell CDEF has also the symmetry of a new rectangular cell EFGH of dimensions 18.6 Å U × 10.2 Å U × 9.8 Å U, which would show strong reflections from the planes separated by 4.65 Å U and 3.4 Å U, respectively, the 9.8 Å U spacing not being changed.

ABCD would show strong reflections at spacings 5.1 Å U with weaker ones at 1.7 Å U known to be present according to the X-ray spectrum photograph. The 6.8 Å U spacing indicated by this diagram is not clearly indicated in the X-ray spectrum but it cannot be said to be absent.

In Diagram 2 there is shown another way in which alpha Keratin could be transformed to beta Keratin. In this case the monoclinic form is produced by moving the atoms A and B with respect to B and C to new positions E and F. ABCD again represents the rectangular cell of alpha Keratin and EBCF represents the monoclinic cell of beta Keratin which possesses the symmetry of the rectangular cell EBGH. In this case while lengthways spacings of 3.4 Å U are indicated the rectangular cells of dimensions 18.6 Å U × 10.2 Å U X-rays would not

show them oriented with respect to the fiber axis hence the result would in general be that of disoriented beta Keratin.* As the fiber axis lies along the line AB the transformation of alpha to beta Keratin in this way requires a reduction in the length of 33-1/3 per cent. The first diagram indicates how the transformation from alpha to beta Keratin might occur, by an extension of 100 per cent if the single crystals are 20.4 Å U long and 33-1/3 per cent if the unit crystals are 61.2 Å U long and negligible if the unit crystals consist of large numbers of cells in a line. The second diagram shows how the same change could occur by a contraction of 33-1/3 per cent.

It is clearly seen from these diagrams that the calculated dimensions are entirely in agreement with the observed spots in the X-ray spectra of alpha and beta Keratin. It is also clear that only two symmetrical forms of Keratin are possible whereas for folding molecules with the range of elasticity from —30 per cent to +100 per cent quoted by Astbury and Woods at least three forms should exist, and suitable constitutional formulae for these three forms have already been confidently advanced by Astbury and his colleagues[24]. The deformation from one crystal form to another may take place quite gradually yet the X-ray spectra would show no gradual change in dimensions because no reflections would occur in the intermediate stages; one would either have reflections at multiples of 5.1 Å U (including 1.7 Å U) or multiples of 3.4 Å U. Thus one does not need to assume a sudden transformation from one form to another as do Astbury and his co-workers: the smooth load extension curve which is quoted so often indicates no such sudden changes.

The different ways in which the transformation can take place according to the diagrams are quite in conformity with the observations that alpha Keratin can be converted to beta Keratin by stretching the fibers from 30 per cent to 100 per cent, by compressing the fibers laterally or by treatment with boiling sodium bisulfite which causes the fibers to shrink about 30 per cent during drying and produces disoriented beta Keratin.

With this explanation there is no need to assume the existence of some new and hitherto unkown form of molecule in Keratin fibers which can fold itself up at atomic distances in such a convenient way as to prefer specific dimensions the very existence of which demands a higher degree of rigidity, than is consistent with its elasticity. There is no *a priori* reason why such a molecule should not fold up still further and produce a third form of Keratin, hence there is no reason why such an elastic molecule should select two main dimensions and show no intermediate ones. However, no third form of Keratin has been discovered.

The agreement between the observed date and those deduced from the two forms of crystal—rectangular and monoclinic shown in the diagram is so remarkable that the writer has no hesitation in regarding this explanation as the true explanation of the existence of two and only two forms of Keratin, the inter-conversion of the one to the other being undoubtedly independent of the elasticity of the whole fiber which is controlled by that non-crystalline portion which constitutes the bulk of the Keratin fiber.

An examination of the diagram shows that the volume of the unit cell becomes reduced by one-third, corresponding to an increased density of 50 per cent. If the fiber consisted entirely of these unit crystals such a change could only occur by the formation of spaces between the crystals. But to quote Astbury and Street[25], "The lengthy exposure required for good hair photographs is an indication that only a fraction of the hair is in a true or approximately true crystalline state and from what we know of amorphous X-ray halos would lead us to expect a diffuse reflection of the kind observed. Amorphous halos tend to reveal the "most probable" inter- or intra-molecular distances in a non-crystalline state; and the non-crystallir fraction of the hair substance, being built of combinations of alpha amino acids which must have certain relatively small spaces in common would naturally yield such a halo."

From such statement one must conclude, therefore, that the increased density of that fraction of the hair which is crystalline is balanced by some opening out or breakdown of the non-crystalline constituents which should render it more liable to chemical attack. That stretched hair is more easily attacked by chemicals has been clearly stated by Astbury and Street[26]. Similarly, hairs which have been boiled in sodium bisulfite solution, which converts alpha to beta Keratin, are much more easily attacked by other chemicals than is normal hair.

THE PHYSICAL PROPERTIES OF KERATIN FIBERS

A very thorough investigation of the load extension curves of the Keratin fibers was first made by Speakman[27], and the effect of humidity, temperature and time were noted. With increasing humidity wool stretches further and more easily. In the presence of water wool stretches further and more easily as the temperature increases but the breaking strength of the fiber decreases.

Under constant load the extension of the wool fiber increases with time rapidly at first and gradually becoming slower.

Speakman was able to show that if hair is stretched in water up to an extension not exceeding about 30 per cent, then allowed to recover its original length by contact with water for 24 hours, the load extension curve could be exactly repeated. But if the hair is stretched more than 30 per cent, the load extension curve can never be repeated, less work is required for the second extension. This permanent internal breakdown increases as the extension increases also with the number of times the fibers are stretched beyond 30 per cent as well as with the time the fibers are kept in the stretched position.

*The primary crystals are arranged around the cylindrical fiber.

The load extension curves of hair and wool are modified when the fibers are treated with steam for a short time under tension followed by a further period of steaming without tension. This effect is more marked if the fibers are stretched about 100 per cent in one per cent caustic soda solution and then released and washed. In this way fibers showing a smooth load-extension curve are obtained, but the fibers are weakened. They require much less force to extend them and break at a lower tension. From this it would appear that some of the internal structure of the fiber has been broken or disintegrated. From this collection of valuable experimental data the following important facts appear: When Keratin fibers are stretched above 6 per cent and more particularly above 30 per cent there is a decay of tension with time and this decay occurs more rapidly when moisture or water is present.

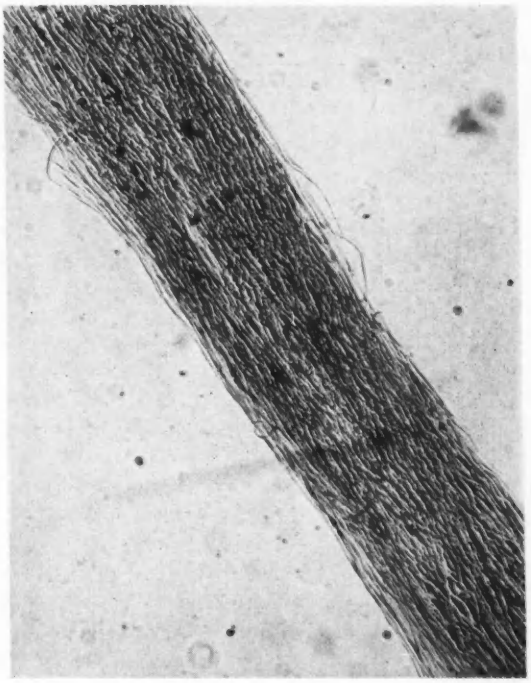
When stretched fibers are released there is at first a rapid contraction followed by a slow one and the rate of contraction depends on the amount of moisture or of water present. In the absence of water complete restoration to the original length does not take place. The so-called generalized load load-extension curve is only attainable in the presence of water. It is perfectly clear from this that water is absolutely necessary to the attainment of that elasticity which Astbury and his colleagues associate with changes in X-ray spectrum. This being the case, it is perfectly obvious that water must play a very important part in the changes which take place when Keratin fibers are stretched and released. The only possible way in which this can occur is that water must be absorbed while the fibers are contracting and pressed out when the fibers are being stretched. The rate at which the water may be absorbed by contracting fibers depends on the permeability of the outer surfaces and cell walls, the swelling power of the interior structure and the resistance offered by the more rigid parts of the fibers to this swelling. The rate at which the water may be removed on stretching depends on the tension applied, the avidity of the interior parts for water and the permeability of the outer surface, and cell walls. When fibers are steamed for a short period under tension or treated with caustic soda the swelling power of the interior substances is increased and rigid proteins originally offering much resistance to swelling are broken down and it is quite possible that the permeability of the outer surfaces and cell walls is increased. It is a fact that fibers treated in this way can be easily and rapidly stretched and when released contract much more rapidly than untreated fibers. Since, however, the elasticity is absolutely dependent on the presence of water and must therefore be controlled by the swelling properties of the Keratin within the fibers this elasticity must be regarded as osmotic elasticity and not the true elasticity one associates with rubber which changes its volume less than 2 per cent for an extension of 4000 per cent and without the presence of a solvent or swelling agent. Any permeable elastic tube filled with swellable material must exhibit osmotic elasticity. Thus a fiber composed of an elastic cuticle or outer skin and a swellable cortex would exhibit this property. Similarly, any connected system of elongated cells with their long axes approximately arranged in a line would behave in the same way if these cells consisted of elastic cell walls filled with swellable material. The elastic properties of wool have already been explained as due to elastic cell walls by Speakman[27] who has since[28] abandoned this idea in favor of the extensible chain theory of Astbury without apparently realizing that the elasticity of steam-treated or caustic soda-treated fibers upon which Astbury based his theory was not the true elasticity of a continuous molecular structure. Whether the osmotic elasticity is controlled by an elastic cuticle or by elastic cell walls might be decided by studying the elastic properties of descaled fibers. If the elastic properties of descaled fibers should prove identical with those of ordinary fibers then the cuticle is not entirely responsible for the elastic properties. Nevertheless from the work already done with descaled fibers and with fibers treated with sodium sulfide it is clear that the cuticle does play some part in the properties of the Keratin fibers.

X-ray spectra of different forms of Keratin provide no reliable evidence to explain the properties of normal and chemically treated Keratin fibers.

The microscope is useful in learning the structure of hairs after treatment with swelling and other reagents. Astbury and Street[29] have shown that if hair is loaded with a small weight of about one gram and placed in a 1 per cent solution of sodium sulfide the hair stretches to about double its length before breaking. It is very easy to show that at this stage the load is borne by the swollen cuticle or outer layer or layers of the hair. The cortex oozes out of the cuticle either at the open ends or from any part of the fiber which has been ruptured. In the microscope under dark ground illumination the portion which oozes out is seen to consist of fine particles of elongated shape suspended in a clear solution. The cuticle or outer portion when examined by dark ground illumination is seen to be of net-work structure (Fig. 3) and has not that fibrillar (Fig. 4) form which can easily be shown in the cortex by treating descaled hairs with sodium sulfide and in many other ways. The cuticle has been stated by Astbury and Street to give an X-ray spectrum different from that of the cortex. Hence when hairs are descaled the X-ray spectrum becomes more distinct. When the outer layers or cuticle are separated from the fibers by the action of sodium sulfide it is found to be very elastic. When stretched it shrinks widthways and when expanded widthways it contracts lengthways. Neither X-rays nor the microscope provides any explanation of the great elasticity of these outer layers but from the fact that the surface of Keratin fibers is never smooth there is a definite possibility that there are present in it microscopic folds or puckers which become straightened out somewhat when the cuticle is expanded. It is possible that the cell walls

116X

Fig. 3.



116X

Fig. 4.

of the ultimate spindle-shaped cells known to be present in hair and in wool may have similar properties and a similar structure to the cuticular layers. The writer is strongly in favor of Speakman's view that "the elastic properties of the fibers as a whole are those of the single cell which consists of an elastic cell wall enclosing a fibrillar structure whose interstices are filled with a viscous medium."

SUPER-CONTRACTION

In 1928 Speakman[27] observed that fibers which had been permanently set in steam were released in caustic soda or in sodium sulfide solution and after drying were found to have shrunk below their original length.

In 1932 Astbury and Woods[30] observed that fibers stretched 50 per cent and while under strain steamed for 2 minutes then released in the steam and steamed for some time contracted below their original length by about 10 per cent. A further contraction to 30 per cent occurred in drying. The X-ray spectrum of fibers treated in this way differed from those of normal fibers in such a way as led to the suggestion that certain spacings at right angles to the axis had undergone some widening or breakage[31] whereby the backbone chains of the fibers folded up to smaller dimensions than those found in the Keratin of unstretched hair and wool. No change in lengthways spacing which should arise in consequence of this has yet been observed. This super-contraction can be produced in other ways[32] such as by boiling the fibers in sodium bisulfite, in potassium cyanide solution or in concentrated silver sulfate solution. It may also be produced in the cold by sodium sulfide solution. The following equations[33] have been given in explanation of these effects:—

$$R{-}S{-}S{-}R \xrightarrow{Na_2S} 2\,R{-}SNa \quad (33)$$

$$R{-}S{-}S{-}R \xrightarrow{NaHSO_3} R.SNa + R{-}S{-}SO_3H \quad (34)$$

$$R{-}S{-}S{-}R \xrightarrow{KCN} R{-}SK + R{-}SCN \quad (35)$$

$$3\,R{-}S{-}S{-}R \xrightarrow[3H_2O]{Ag_2SO_4} R{-}SO_3 + 5R{-}SH. \quad (36)$$

Chemical evidence from the super-contracted fibers has not, so far, been produced.

Super-contraction can also be produced by boiling Keratin fibers in a 10 per cent solution of formic acid for 30 minutes, or treating in a hot concentrated solution of zinc chloride for 30 minutes[37] or by boiling in normal hydrochloric acid for 3 hours[38] in which case 18 per cent super-contraction occurs. None of these reagents has the property of splitting up disulfide linkages. Speakman[38] considers, however, that these reagents hydrolize the main polypeptide chains.

Sodium sulfite[39] is known to act on cystine in a similar way to sodium bisulfite but does not cause super-contraction. In order to account for this Speakman[40] considers that to cause super-contraction not only the disulfide link-

ages must be broken but the salt-linkages must also be acted upon and the acidity of bisulfite causes it to act on the salt linkages as well as on the disulfide linkages. Speakman does not, however, explain why the neutral potassium cyanide should cause super-contraction even though it does not act on salt linkages. Hence we see that it is possible to cause super-contraction by some neutral substances which react with disulfide linkages but not with salt linkages; by acidic substances which attack both disulfide linkages and salt linkages, by acidic substances which attack main polypeptide molecules and possibly also salt linkages. Yet in sodium sulfite we have a neutral substance which attacks disulfide linkages and produces no super-contraction. It becomes clear, therefore, that we have not yet arrived at the stage where a proper chemical explanation of super-contraction can be produced. It may be mentioned here that Astbury uses super-contraction as evidence of the existence in normal Keratin of long chain molecules having contractible properties while Speakman uses this deduced hypotheses to explain super-contraction. Such methods of argument lie outside the range of sound logic and by arguing in a circle prove nothing.

The case of sodium bisulfite is of considerable importance: hairs which have been boiled in 5 per cent sodium bisulfide for half an hour or one hour do not super-contract, they swell considerably widthways and slightly lengthways. Super-contraction occurs only when the swollen fibers are dehydrated or deswelled in some way. Thus when the fibers are dried in air they shrink about 30 per cent. When placed in absolute alcohol they shrink 12 per cent in less than 5 seconds and undergo a further shrinkage to 18 per cent on air drying.

When bisulfite treated fibers are placed in a 10.4 per cent solution of sodium sulfate they super-contract 14 per cent (Private communication from Dr. Speakman). In the boiling of the fibers with bisulfite the chemical reaction and the swelling necessarily starts on the outer surfaces first and gradually penetrates to the interior. If we are to reverse this swelling process in the correct order we should deswell the interior first and the outer surfaces last. This reversal cannot, however, be effected. Deswelling by alcohol or by salt solutions necessarily commences with the outer surfaces and evaporation of water in air necessarily starts from the outer surfaces. If within the fiber itself there are proteins such as cell membranes which are less swollen possibly due to a higher degree of polymerization than the remainder of these proteins would normally be dehydrated first.

An attempt was made by the writer to avoid this prefential evaporation from the surface by placing the fibers, after boiling half an hour in 5 per cent sodium bisulfate solution and washing, in air-free water, in a vacuum-flask containing cold water and rapidly creating a vacuum high enough to boil the water in the flask and within the fiber. It was observed that the super-contraction was reduced to 2 per cent while the other fibers treated simultaneously in the same bisulfite solution super-contracted 22 to 25 per cent when dried slowly in contact with air. When the boiling in bisulfite was continued for 1 hour the super-contraction in air was approximately 30 per cent while the super-contraction by the vacuum drying method remained from 15 to 20 per cent. Based upon this experiment the writer put forward the hypothesis that super-contraction was caused by the mechanical interaction of the cuticle and cortex during the processes of swelling and shrinking. Thus, in general, super-contraction could occur when the cortex hydrates or swells more or more rapidly than the cuticle or when the cuticle shrinks more or more rapidly than the cortex.

In a private communication Speakman has informed the writer that descaled fibers super-contract on air-drying after boiling in 5 per cent sodium bisulfite for 1 hour, in exactly the same way as normal fibers and that the effect is dependent upon the extent of descaling. This evidence shows that whatever part the cuticle may play in the super-contraction by bisulfite it cannot be of primary importance. Nevertheless, as indicated above, elongated spindle shaped cells with elastic cell walls would behave in exactly the same way as a long cylindrical fiber with elastic cuticle and it is possible that the super-contraction may be caused by the mechanical interaction of the elastic cell-walls of ultimate spindle-shaped cells and the swellable contents of these cells.

Considering now the super-contraction produced by sodium bisulfite from a chemical point of view. According to Speakman the following reaction takes place:

$$R—S—S—R \xrightarrow{NaHSO_3} R\text{-}SNa + R\text{-}S.SO_3H$$

The sodium bisulfite here exercises a reducing action with the production of one molecule of R.S.Na. It is noteworthy that a sodium phosphite or sodium hypophosphite solution made up to contain the same equivalent of sodium and the same pH value does not produce any super-contraction when hair fibers are boiled in it for half an hour. Yet sodium phosphite especially in acid solution is a much more powerful reducing agent than is sodium bisulfite.

When hair or wool is boiled for half an hour in 5 per cent sodium bisulfite it is not possible to detect the presence of S.Na groupings which may easily be found in stretched steamed wool by the use of silver or mercurous salts. As a matter of fact many organic compounds containing S.Na groups are oxidized by an excess of sodium bisulfite. The reaction proposed by Speakman is, therefore, very doubtful. The writer is of the opinion that the bisulfite may form additive compounds with the Keratin, leading to much swelling without disruption of the disulfide groups. This would account for the fact that when fibers, boiled in 5 per cent sodium bisulfite and dried in a vacuum under such conditions that the freely hung fibers do not shrink appreciably, are boiled in water for half an hour no more change is produced than occurs with normal fibers not treated with bisulfite.

In order to explain why neutral sodium sulfite does not produce super-contraction Speakman states that sufficient acidity is needed to act also on the salt linkages and presumably to react with free amido groups to form a salt with sulfurous acid. The destruction of those amido groups either by de-amination or by reaction with quinone, etc., enables sulfite to cause super-contraction. Now the effect of this acidity of the bisulfite is to cause swelling and if we accept Speakman's view, this swelling is due to the combination of the free amino groups with sulfurous acid after or simultaneously with the breakdown of disulfide linkages which normally would restrain or prevent the swelling. The point then arises, is it the action of the acid on some salt-linkages which finally removes any resistance to the contraction of contractile molecular chains to produce super-contraction or is it the swelling followed by irreversible de-swelling which is the important factor. If it be the action of the acid on some salt-linkages then any process which reverses this effect should have the entirely opposite effect of super-contraction. Yet sodium sulfate which decreases the swelling and therefore reverses the effect of the acid, actually causes the super-contraction to take place.

On the other hand if the sodium sulfate is added to the 5 per cent sodium bisulfite so as to make a solution containing $\frac{M}{1}$ — sodium sulfate and the pH value adjusted to the same figure as the 5 per cent sodium bisulfite alone, fibers boiled in the solution for half an hour do not super-contract on washing and drying in air. From this it is quite clear that a reagent which acts upon disulfide compounds and has a pH value high enough to act on salt linkages does not produce super-contraction unless free swelling is permitted.

It may be mentioned here that fibers boiled half an hour in 5 per cent sodium bisulfite super-contract 14 per cent in cold $\frac{M}{1}$ — sodium sulfite solution while on air-drying before or after removal of the sulfite super-contract further to 22 per cent, in other words practically the same as when sodium sulfate is used. If the dried super-contracted fibers are placed in sodium sulfite they extend about 10 per cent and return to original length when air-dried. The same fibers placed in pure water extend to 19 per cent above their original fully-contracted dry length corresponding to a residual super-contraction in the wet state of 7 per cent of their original natural length. That these length changes are determined by swelling phenomena cannot be doubted.

It should be mentioned here that super-contraction can take place in two entirely different ways. Thus with fibers which have been steamed under tension for 2 minutes, or fibers which have been stretched in caustic soda or given permanent set and afterwards treated with caustic soda or sodium sulfide, super-contraction is accompanied by the inhibition of water by the Keratin fiber. In the case of bisulfite treated fibers and fibers swollen in other ways such as by boiling in 10 per cent formic acid or treating in hot concentrated zinc chloride solution super-contraction is accompanied by a loss of water. In accordance with the general phenomena associated with osmotic elasticity, in the first range the swelling proteins would produce a pressure within the cell walls of spindle-shaped cells and cause them to shrink lengthways, and in the second range the shrinking cell-walls would create a pressure against the still swollen contents resulting also in a lengthways shrinkage of the cell walls.

It is interesting to note here that when Keratin fibers are boiled in bisulfite the alpha Keratin is converted to beta Keratin which in super-contracted fibers appears in a disoriented condition, the shrinkage in length being around 30 per cent.

An examination of the diagram (Fig. 2) will show how the crystals of alpha Keratin oriented mainly about the fiber axis could easily be converted into the monoclinic form having two kinds of symmetry—rectangular and monoclinic — the rectangular form being not oriented around the axis, the length contraction being 30 per cent.

If this be the explanation of the super-contraction caused by bisulfite it becomes very difficult to explain the effect of drying the bisulfite-treated fibers in a vacuum in an atmosphere saturated with water: although many of the other facts connected with the super-contraction by bisulfite are quite in agreement with the idea. To reconcile this explanation of super-contraction with the results of the vacuum drying experiments one would have to introduce other assumptions few of which are capable of direct proof.

The data and arguments just put forward are all definitely against the hypothesis of the existence in normal Keratin of contractible polypeptide chains. The chemical data are in favor of the view that the swelling essential to super-contraction is partly controlled by the cystine content of Keratin, partly by the presence of reactive groupings such as amido and carbon groups and also, perhaps to a lesser extent, by the amido-acid constitutents of the polypeptides present in Keratin. Undoubtedly the sulfur linkages play a very important part in the swelling phenomena and in all those phenomena arising out of the swelling and of the subsequent deswelling. There can be no doubt that super-contraction is a special case of swelling phenomenon. It cannot be produced if swelling is prevented even though there are present all the chemicals needed to attack disulfide linkages and salt linkages.

PERMANENT SET

The first attempt to explain the phenomenon of permanent set of wool was made by the writer in 1918[41].

Knowing that rubber becomes doubly refracting when stretched and that the same effect can be produced with substances such as gelatine attempts were made to utilize polarized light to investigate the changes in wool when

given permanent set. An unsuccessful attempt was made at the time to ascertain by means of X-rays whether crystallization was caused by the stretching[42]. It was observed that when hair and wool are stretched a pronounced increase takes place in the illumination given between crossed nicols in polarized light, the fibers being placed at an angle of 45° to the plane of polarization. This effect persists if the fiber is given what is called temporary set but disappears if the fiber is given permanent set, from which it was concluded that the strains produced within the fiber substance by stretching remain dormant when the fiber is given temporary set but are dispersed when the fiber is given permanent set.

While it is nowadays considered that the double refraction imparted to isotropic materials by deformation is due to orientation, this does not in any way alter the fact that polarized light can be used to detect a strained condition in many isotropic substances. No attempt was made in 1918 to ascertain how the strains were removed during permanent setting but it is clear that either some substance or some chemical bonds holding the structure together must be weakened or disconnected. The position of these substances or chemical bonds can only be determined when the inner structure of the Keratin fibers is fully understood. While it was known at that time that the tension upon the fibers held at any given extended length rapidly fell as the fibers were treated with steam or with boiling water to produce the permanent set no quantitative measurements were made, the work was more or less a preliminary survey.

A more systematic examination was made by Speakman ten years later[43]. In the course of this work Speakman observed that permanently set fibers showed marked contractile properties in steam or in boiling water although they could not be restored to their original length. Thus fibers stretched 50 per cent and steamed for a considerable time contracted in steam but retained 35 per cent of permanent set. Speakman also observed that this permanent set was released when the fibers were placed in caustic soda or sodium sulfide and shrinkage proceeded below the original length. It should, however, be pointed out that permanently set fibers shrunk by these reagents become permanently damaged, although they can be restored to their original length they do not regain their original properties nor does the beta Keratin revert to alpha Keratin. The following optimistic statement of Astbury's[44] was not confirmed:

"Furthermore—and this is a striking example of the power of X-ray methods even in such difficult fields as are offered by protein structure—it will be shown how the maximum true permanent set which may be deduced from the X-ray data, namely 29 per cent, is, in fact, very approximately the same as the highest permanent set which may be obtained in practice."

Astbury and Woods[45] observed that hair and wool fibers which had been extended at least 50 per cent and steamed showed in the X-ray spectrum photograph a spreading of some of the spots indicating a widening of spacings approximately at right angles to the fiber axis. This observation was regarded as indicating some change in side chains having a direct bearing upon permanent set. Since most of the experiments on permanent set were carried out at extensions of less than 50 per cent at which the spreading of the spots in the photograph is not noticeable this evidence is far from being conclusive.

Speakman[46] showed that in producing permanent set by boiling aqueous solutions the pH value plays an important part. The maximum effect is produced by a solution of pH value 9.2 obtained by using a solution of borax. Appreciable permanent set is produced by half an hour boiling in solutions of pH value lying between 6.5 and 10.0.

Permanent set is said to be prevented by deamination of hair and wool fibers[47]. Thus, normal fibers steamed 6 hours at 30 per cent extension retain 20 per cent permanent set after 3 hours boiling in water. The same treatment produced no permanent set in fibers which had been immersed for 2 days in a solution containing 8.62 grams of sodium nitrite, 7.1 cc. of glacial acetic acid and 12.9 cc. of water which is said to deaminate the fiber.

According to Sookne and Harris[48], nitrous acid is an active oxidizing agent and there is evidence that it oxidizes some of the sulfur derivatives present in Keratin fibers.

Astbury and Dawson[49] have shown that fibers deaminated for 42 hours, steamed at 35 per cent extension for a short time and then steamed without tension for some time return to their original length and the beta Keratin present in the stretched fiber returns to alpha Keratin. If, however, the steaming at 35 per cent extension is done for 10 hours the further steaming without tension restores the fibers to the original length but the beta Keratin remains, thus showing that the failure to take permanent set is a phenomenon independent of the changes in crystal structure. Incidentally, it shows that the extensibility of the fiber is also independent of crystal structure because in the one case the crystal structure changes and in the other case it does not, yet in both cases the fibers shrink back to their original length. Thus it becomes clear that permanent set is a phenomenon controlled by the major non-crystalline proteins of the Keratin fibers and any deductions made about permanent set from the change in crystal form indicated by X-rays cannot be accepted.

It has also been observed[50] that quinone treated fibers acquired no permanent set after boiling at 29 per cent extension for 30 minutes in borax solution at pH 9.2. Fibers treated with concentrated silver sulfate or cuprous chloride and washed also fail to take permanent set on steaming[51] but the same effect is not produced by cupric chloride, zinc sulfate or cobalt chloride after washing because these salts are not retained by the wool, they have no mordanting action. A similar effect is produced by oxidizing agents[52] the effect of which is largely counterbalanced by after-treatment with certain reducing agents.

Baryta and caustic soda both extract some sulfur from wool and both reduce considerably the power of acquiring permanent set in steam[53].

Speakman[54] has been able to impart permanent set to wool fibers by stretching in presence of bisulfite of soda the effect being most pronounced at pH 5.95 used at 50° C. for some time.

Permanent set can be imparted at 35° C. if the fibers, after treatment with a bisulfite solution brought to pH 5.95, are treated with barium salts or with oxidizing agents or with both[55].

Similar results are secured by using sodium sulfite brought to pH 10.9 by the addition of alkaline substances such as sodium carbonate and silicate[56].

The view is held[57] that to produce permanent set disulfide links in Keratin must first be broken and the free sulfydrate endings caused to combine together or with free amido endings in new positions.

The removal of sulfur by alkalies is said to prevent such recombination as also does treatment with any substance which itself combines with the sulfydrate endings as may silver and cuprous salts, or which destroys or combines with amido endings as may be caused by nitrous acid, quinone, etc.

In the experiments with Baryta and caustic soda analytical results were obtained which clearly show some parallelism between the amount of sulfur remaining in the wool and the power of acquiring permanent set. In the other cases, however, the chemical effects are deduced from observations on permanent set and supported only by the evidence of analogy with the known reactions of cystine, arginine, etc., in the free state. No chemical evidence from the wool itself is given.

There are many points remaining unexplained. It is difficult to understand why magnesium sulfate exercises a strong restraining action on the permanent setting of fibers in boiling water. Thus fibers boiled half an hour in water at 40 per cent extension were found by the writer[58] to retain 18 per cent permanent set while fibers boiled half an hour in a 5 per cent magnesium sulfate solution retained practically no pronounced set after boiling half an hour in water in each case. In referring to this observation Speakman[59] suggested that the writer had failed to take account of the effect of the pH value in the rate and extent of setting. In Speakman's earlier experiments it was shown that hairs boiled for 30 minutes at 40 per cent extension in solutions of pH values from 6.5 to 10.0 retained from 10 to 20 per cent permanent set after boiling one hour in water yet in replying to the writer's criticism Speakman[60] observed only 0.5 per cent permanent set with 5 per cent magnesium sulfate the pH of which lies between 6.5 and 7.2.

Continued boiling in the magnesium sulfate does produce some permanent set, thus Speakman observed 14.9 per cent in 2 hours. The writer limited the treatment to 30 minutes because longer boiling produces damage to the fiber and probably hydrolysis of the magnesium sulfate.

Nevertheless it is seen that magnesium sulfate although it does not form sulfides in aqueous solution retards very considerably the permanent setting of Keratin fibers.

It is difficult to understand why boiling 5 per cent sodium bisulfite applied for 30 minutes on loose fibers causes super-contraction said to be due to the breakdown of side linkages setting free contractible molecular chains while, when used on stretched fibers for the same time, causes permanent set said to be due to rebuilding of side chains, already broken by the stretching, to new structures resisting the contraction of such chains. The two effects appear contradictory and cannot both support the folding-molecule theory.

Quinone behaves in a different way, it causes normal fibers to be easily super-contracted but prevents stretched fibers from acquiring permanent set by boiling in borax solution. Similar effects are observed with fibers treated with nitrous acid and with bichromates.

In referring to the action of caustic soda upon permanently set fibers Speakman[61] states that "Fibers which had taken a permanent set in steam *were released in solutions of caustic soda*" whereas in the same publication[62] he stated that "Further, since *caustic soda,* which is capable of attack on cystine linkages, *is unable to break down the linkages characteristic of permanent set* it is unlikely that permanent set is due to the reformation of cystine linkages between the peptide chains." These two remarks are contradictory but another remark in the same journal[63] shows how this arises. "Similarly although set fibers contract in caustic soda solution Astbury has shown that *the contraction does not depend on the reversion of beta to alpha Keratin.*" It is clear that the contradiction arises from the confusion of two different and disconnected effects, the removal of permanent set and the change from beta to alpha Keratin which has nothing to do with it. Caustic soda does remove the permanent set and must, therefore, attack the substances responsible for it whether these are dependent upon special linkages for their activity or not.

The activity of formic acid is of particular interest. Astbury and Dawson[49] state that fibers boiled in water with 20 per cent formic acid on the weight of Keratin do not super-contract when steamed 4 minutes at 50 per cent extension, neither do they acquire permanent set. The writer observed that fibers boiled 30 minutes at 40 per cent extension in 5 per cent solution of formic acid do not acquire permanent set but they do super-contract, about 6 per cent in drying. Unstrained fibers boiled 30 minutes in 10 per cent formic acid super-contract 14 per cent in drying. Concentrated formic acid in the cold causes Keratin fibers to swell laterally and acquire special elastic properties, both effects being removed on washing with water when the fiber returns to its original condition. No super-contraction is caused. Water seems to be an

essential solvent to produce super-contraction thus indicating some hydrolysis as being essential. Fibers boiled 30 minutes in 5 per cent sodium bisulfite, which does not in itself cause super-contraction but induces super-contraction on drying, are caused to super-contract if placed in anhydrous formic acid but not to the same extent as by anhydrous alcohol because the swelling action of the formic acid hinders the de-swelling of the fiber.

The different results produced by anhydrous formic acid and by boiling 10 per cent solution of formic acid do not indicate that super-contraction is due to breakdown of disulfide linkages; they merely confirm the writer's opinion that the phenomena is not yet explicable by chemical reactions of any special type.

Permanent set is reduced when aniline is added to the water[64] although the pH value remains between 7 and 9. Aniline cannot react with amino groups but it might react with sulfide groups. However, quite a number of tertiary amino compounds when added to water prevent permanent set[64] and in some cases cause super-contraction and these compounds do not react chemically with either amino compounds or disulfide or sulfide compounds. In all these cases the pH value remains between 7 and 9.

The activity of various chemical substances in modifying the properties of wool in relation to permanent set is of so varied a character that it is not possible to find one chemical explanation of all of them. It is obvious that permanent set can be caused or prevented by conditions favoring a variety of chemical reactions and if we are to find a common cause for permanent set we must look outside the sphere of pure chemistry.

The most important observation relating to permanent set is the observation of the decay of tension in the fiber during the steaming. This might arise in two ways, firstly by the breakdown of substances or of chemical bonds which bind the fiber together lengthways or by the creation of new linkages to resist the contraction of some molecular chains which have been extended. Now if the latter theory, which is the one adopted by Astbury and Speakman, is correct then during the first two minutes of steaming when side linkages are said to be broken and the resistance to contraction reduced there should be an increase in the tension and the tension should then slowly decay as resistant side linkages are formed. No such initial increase of tension takes place, there is a continuous decay of tension which is, in fact, much more rapid in the first few minutes than later on. The former explanation is, therefore, the more likely to apply to the permanent setting by steam or by boiling aqueous solutions such as solutions of borax. It is agreed that if the substances which bind the fiber lengthways are, after breakdown or swelling, made more resistant to boiling water this would assist the permanent set. Thus, if these substances are reduced and re-oxidized while the fiber is under tension or if these substances are highly swollen or partially dissolved and then rendered less swellable or more insoluble while the fiber is under tension permanent set will be assisted. Nevertheless, the whole question of permanent set is connected with the osmotic elasticity of the fibers referred to in earlier pages. Any process which attacks the elastic cuticle of the fiber or the elastic cell-walls of the spindle-shaped ultimate cells must cause a permanent loss in shrinking power and assist permanent set. Also, if the fibrillar contents of the spindle-shaped ultimate cells are caused to slide while the stretched fibers are treated with steam or other chemicals those spindle-shaped cells will tend to remain extended. Again, if the spindle-shaped cells themselves slide past one another and afterwards become arranged in new positions permanent set will be caused or assisted. It is indeed quite likely that permanent set is due to two causes, weakening of the cell-walls of spindle-shaped cells and/or of the cuticle of the fibers and rearrangement of spindle-shaped cells or of their fibrillar contents in new positions in consequence of swelling processes occurring during extension.

Permanent set may be prevented in several ways. Processes which prevent the swelling of the cuticle and of the walls of ultimate spindle-shaped cells in boiling water should reduce or prevent permanent set. If at the same time the other proteins in the fiber were prevented from swelling again permanent set would be reduced. Processes which attack the intercellular proteins so as to leave the ultimate cells unable to be fixed in new positions would also reduce or prevent permanent set.

The remarkable resistance of the cuticle or scale-sheath of hair and wool to attack by alkalies indicates some difference in constitution, the protein may be more basic in type or of a higher degree of polymerization. It is possible that the cell-wall Keratin is similar in constitution. If these more resistant proteins are of basic type they would be attacked preferentially by reagents acting on amido groups.

The tanning of Keratin fibers with quinone reduces their tendency to swell in water and it is thought that the quinone reacts with the basic groups to reduce the acid combining capacity and with other parts of the fiber to reduce the swelling which occurs in pure water. Quinone prevents the permanent setting of Keratin fibers by steam.

The action of nitrous acid is not limited to deamination. It exercises oxidizing action on sulfur derivatives. Nitrous acid decreases the swelling in acid solutions of pH 4 but increases the swelling in neutral or alkaline solutions and is likely to attack the intracellular Keratin. Treatment of hair and wool with nitrous acid destroys its power of acquiring permanent set in steam.

Baryta and caustic soda remove from Keratin some of the sulfur but it is apparent from the loss in weight that protein substances are also removed. It has been shown that the sulfur which is split off from the wool is in the form of inorganic sulfides and the suggestion has been made that the labile sulfur comes from the formation of a sulfur compound other than cysteine which is itself rela-

tively stable to alkalies. Recently (Nature, 1938, 141.118) Speakman, has shown that the intercellular protein in Keratin fibers is deficient in sulfur.

The action of alkaline solutions upon the Keratins is generally of a destructive nature and much remains to be learned before we could offer any reasonable explanations of their effect or permanent set. The alkalies may act on the intercellular protein in such a way as to prevent ultimate spindle-shaped cells from being fixed or cemented in new positions or it may attack the fibrillar contents of those cells.

Reviewing the data collected in this paper it appears that from X-ray spectrum photographs, which are so far from distinct as to show quite clearly that only a small fraction of the Keratin fibers can possess crystalline structure, an elaborate theory of molecular transformations has been developed by Astbury and his co-workers, which, had the Keratin fibers consisted entirely of single crystalline substances would still not be justified by the evidence available.

The very necessary presence of water to produce that elasticity upon which so much of the argument depends has not been overlooked but its very important influence on the argument has not apparently been considered. The contradictory nature of the evidence provided by much of the experimental work of the Leeds school, instead of being accepted as contradictory has been interpreted so as to bring it all in line with the preconceived ideas underlying the whole of the voluminous communications published up to date. Thus, it is known[20] that Keratin fibers can be deformed without changing the crystalline structure and that the crystalline structure can be changed without deforming the fiber yet both these phenomena are interpreted as particular cases of the general idea that the crystal form is positively related to the deformation of hypothetical elastic molecules for the existence of which there is no evidence except that of the elasticity of the fibers it is sought to explain.

Similarly the evidence of super-contraction is first taken by Astbury to indicate positively the existence, in normal hair and wool, of contractile molecular chains controlled by side-chains the existence of which has been presumed from a small change in X-ray spectrum produced in some unknown constituent of the fibers by the very opposite process of extending the fibers 50 per cent.

With this idea of Astbury's Speakman proceeds to explain the super-contraction from which the idea was originally and erroneously deduced. Furthermore, to provide evidence for the existence of side-chains Speakman quotes experiments on super-contraction without apparently realizing that the existence of such side-chains has never been proved and that one cannot reasonably assume the proof to provide the assumption. The writer cannot help but appreciate very much the painstaking experimental work carried out by the Leeds School but cannot appreciate the "logical merry-go-round" methods of argument used. Even quite recently Speakman[67] has produced evidence that cross-linkages *are* formed which consists entirely of an experiment upon super-contraction from which no sound logical conclusions can be drawn.

The writer's object in criticizing this work so severely is to endeavor to reduce the speculation and to bring the whole subject within the sphere of sound logic in the hopes that others might be encouraged to investigate the subject in a fuller manner discarding for the time being any speculative hypotheses however attractive they may appear. Until the chemical constitution of each constituent of the Keratin fibers is known and the influence of each physical and chemical constituent upon the various properties of these fibers determined no satisfactory chemical or physical explanation can be obtained.

The following is a summary of the points discussed in this paper:—

1. Since only a fraction of the substance of Keratin fibers is in a true or approximately true crystalline state the properties of hair and wool can at the most be only partially influenced by the crystalline form.
2. That the changes in the X-ray spectra which can be produced in hair and wool in a variety of ways are not directly related to their elastic properties.
3. That the transformation from one crystal form to another is most likely due to the deformation of crystals of rectangular form to crystals of monoclinic form of the same length of sides and vice versa.
4. That Statement (3) accounts satisfactorily for the fact that the change in crystal form can be produced by stretching lengthways by compressing widthways and by chemical treatment resulting in lengthways shrinkage.
5. That the hypothesis of extensible molecular chains advanced by Astbury and his co-workers was deduced from inconclusive and insufficient evidence and is untenable. It does not explain all the known facts.
6. That the idea that the molecule of Keratin in normal unstrained hair and wool has contractile properties is unsupported by any conclusive evidence and is untenable.
7. That the elastic properties of Keratin fibers modified by the action of caustic soda or of steam under certain conditions, is not the true elasticity possessed by rubber but is osmotic elasticity largely influenced by the absorption and desorption of water by the proteins within the fiber and within the unit cells of the fiber.
8. That the properties of wool are accounted for by Speakman's theory according to which the elasticity is controlled by elastic cell-walls while the "plasticity" is controlled by the fibrillar contents of these cells as well as by the viscous or colloidal interfibrillar substances.

9. That super-contraction is not due to the presence of contractile chains in Keratin fibers but is due to the interaction of the elastic cell-walls and their swellable contents, and is a special case of swelling phenomena.
10. That super-contraction takes place in two general ways, one accompanied by swelling and associated with the osmotic elasticity and the other accompanied by volumetric contraction of the swollen protein both resulting in lengthways shrinkage.
11. That the change in crystal form which is produced when Keratin fibers are super-contracted by sodium bisulfite agrees with a change from oriented rectangular crystals to monoclinic crystals having the same symmetry as disoriented rectangular crystals and leading to a shortening of the crystals by 33-1/3 per cent in the direction of the fiber axis.
12. That permanent set is not due to or controlled by the conversion of alpha Keratin to beta Keratin although frequently accompanied by this change in the small fraction of crystalline proteins nor is it due to the rebuilding of side linkages between contractile molecular chains in these crystalline proteins which represent only a small fraction of the whole fiber.
13. That permanent set is due to two general causes, one due to the weakening of elastic cell-walls or other structures normally resisting extension and the other due to coagulation or setting of the colloidal cell contents while the fiber is held in a stretched condition.
14. That chemical reactions play an important part in all the swelling and deswelling phenomena associated with Keratins and only in that way do such chemical reactions play a part in super-contraction, permanent set and in other properties of the Keratin fibers.

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